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IDENTIFICATION OF IGNITION CRITERIA  
FOR LOW VULNERABILITY PROPELLANTS

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Veritay Technology, Inc.

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13. ABSTRACT (Maximum 200 words)  This project involved three phases: measuring the heat and pressure generated by various igniter systems, evaluation of the ability of these systems to ignite Lova in a closed bomb, and finally, sampling and analysis of the low pressure combustion products of Lova propellant. The primary goal of this work was to develop a diagnostic methodology to design and evaluate igniter materials for Lova propellants. To measure the heat output and pressure generated by the various igniter materials, a closed bomb was fitted with an instrumented copper liner to serve as a calorimeter. Pellets were made of each formulation, loaded into a primer tube and fired in the calorimeter. Later, tests were done igniting both small and large grains of Lova propellant with the primers characterized above. Ignition time and the reproducibility of the ignition time were measured and compared to the measured heat output and theoretical values for temperature, oxygen content and condensed phase content. The results show that a balance between heat content, oxygen production and condensed phase fraction is needed to get good, reproducible ignition of Lova propellant. Ignition time may be closely related to heat content, but reproducibility increases with oxygen content. The gaseous combustion products sampling experiments were done by using the rupture disks designed to fail at various pressures allowing the venting of the combustion products into a large vessel. Gas samples were analyzed using gas chromatography. These preliminary test results showed that the use of an igniter which has significant oxygen content drives the combustion products of the Lova propellant toward completion, i.e., equilibrium.				
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## FOREWORD

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## Section I

### Ia. INTRODUCTION

#### *Overview*

Low vulnerability ammunition (LOVA) gun propellants are specifically designed to resist unwanted ignition stimuli, and, as a result, are inherently more difficult to ignite than conventional gun propellants. In order to overcome these ignition problems, it is necessary to define the chemical and physical environments which enhance the ignition of these propellants. Once defined, a suitable igniter system can be designed to meet these criteria. It is, therefore, the goal of this program to define the parameters of potential igniter systems which act to produce superior ignition characteristics for a LOVA formulation, and to specify a prospective LOVA igniter material(s).

This program was funded as a Phase I SBIR by the Naval Ordnance Station, Indian Head, Maryland (NOSIH). As a direct result of the program goals, a testing procedure which allows the chemical nature of LOVA propellant combustion products to be identified at low pressure (ignition) conditions has been developed. In addition, potential igniter formulations were investigated using the NASA-LEWIS thermochemical code (version CET86) and promising candidates were produced. A test program was conducted which evaluated the efficacy of these materials, relative to one another, in igniting a LOVA propellant formulation. This included comparisons of heat and pressure outputs, as well as the relative ignition effectiveness of the formulations. Finally, tests were conducted to ascertain the chemical environment present during the low-pressure ignition portion of the propellant combustion cycle, and the effect of a promising ignition system on the chemistry of these combustion gases.

This report is organized into two sections. Section I contains: an introduction, which includes background information pertaining to the problem; a summary of the results of the program; and the conclusions reached as a result of the program. Section II consists of: a description of the experimental apparatuses and techniques utilized; the results obtained from the various experimental approaches utilized during the effort and a discussion of these experimental results; and recommendations for future work in this area.

*Background*

In order to decrease the threat to both Naval ships and servicemen caused by inadvertent ignition of propelling charges and rounds, whether from external or accidental internal stimuli, the Navy, along with the other branches of the armed services, is developing insensitive munitions to replace existing ammunition. In May of 1984 the Chief of Naval Operations (CNO) issued a directive which states that all shipboard munitions would be classed "insensitive" by the year 1995. In May of 1985, the Naval Sea Systems Command (NAVSEA) issued instruction 8010.5, the technical requirements for insensitive munitions. Insensitive propellants are necessarily more difficult to ignite by accidental means; however, as a result, they are also more difficult to ignite in the gun chamber. In order to meet the directive, igniter systems which are safe, reliable and reproducible must be developed and tailored to the specific insensitive propelling charges they are intended to ignite.

Conventional gun propellant formulations, containing one or more nitrate esters, are relatively easy to ignite. Ignition occurs when the propellant surface temperature reaches about 170 °C. Many standard igniter systems employ materials which produce substantial condensed phase, in addition to gaseous, combustion products (e.g. black powder and  $\text{BKNO}_3$ ), so that reliable and reproducible ignition occurs over a wide range of temperatures. Once ignition occurs, flamespread develops immediately and proceeds rapidly through the propellant bed. For conventional propellants, igniter chemistry does not seem to be a significant factor, as these propellants are formulated to develop and sustain the exothermic combustion reaction (even at low pressures) without requiring species from outside sources (igniters).

LOVA propellants, by their very nature, are designed to resist ignition stimuli, and exhibit poor combustion and flamespread under low pressure conditions. The general recipe for LOVA propellants consists of a nitramine particulate (usually RDX) in a continuous binder phase. The binder itself may contain energetic constituents to aid in the combustion process. It has been shown in hot fragment-conductive ignition testing (HFCIT), that conductive heating alone may not be enough to ignite LOVA propellant. In these tests, a hot metal sphere, ranging in size (or mass) and temperature, is dropped into a container of propellant. An ignition temperature is then determined for each sphere size, with larger spheres requiring characteristically lower temperatures for ignition, as a result of their greater thermal mass. In many cases where propellant ignition does not occur, the hot ball merely melts through the bed of propellant, producing dark gaseous decomposition products. These products may be ignited by a secondary ignition source after mixing with air, but the strong ignition source represented by the sphere is not sufficient to ignite the propellant alone. However, when conventional propellant formulations are subjected to the same conditions, the propellant ignites immediately and

burns rapidly. This example underlines some common observations regarding LOVA propellants. These are: a strong ignition source alone may not be enough to rapidly and reproducibly ignite LOVA propellants; an external source of oxygen (or other chemical constituents) may be required to readily obtain ignition of the material; the thermal decomposition process of LOVA propellants is not sufficiently exothermic to sustain combustion.

Some general observations regarding LOVA propellants may be made. The major energetic constituent, RDX, is an attractive candidate for insensitive munitions due to its high chemical stability and explosive energy (greater than that of TNT). When compared to other energetic components of gun propellants, such as nitroglycerine and nitrocellulose, RDX is oxygen poor. For the same mass of material, nitrocellulose (13.5% N) contains 36.0% more O atoms and nitroglycerine 46.7% more O atoms. Therefore, a typical LOVA propellant containing RDX will most likely be oxygen poor when compared to single and double-based propellant formulations. This lack of oxygen leads to an increased CO concentration in the combustion products, when compared to conventional propellant.

The apparent lack of oxygen associated with LOVA propellants has led to the incorporation of large quantities of oxygen-containing species such as  $\text{KClO}_4$  and  $\text{KNO}_3$ , among others, into booster mixes. In this way, it is hoped that the presence of external oxygen can influence the combustion reactions occurring at low pressure, liberating the stored energy which otherwise would not be released until a higher pressure was reached. Pressure affects all propellant combustion, causing a compression of the thermal boundary layer in the combustion gases, which then accelerates the combustion rate leading to even higher pressure levels. However, LOVA propellant combustion appears to be affected by a low pressure level to a much greater extent than are conventional propellants. At low pressures, LOVA propellant combustion is slow, and flamespread does not proceed rapidly. This again may be due, at least in part, to the chemical stability of the RDX molecule.

The mechanism of RDX decomposition is extremely complex, and a consensus opinion has yet to be reached. Some investigators<sup>1</sup> suggest a mechanism in which a single nitro group is cleaved from RDX, leaving a radical which is free to react with NO forming MRDX (mononitroso-RDX) or to simply decompose into  $\text{H}_2\text{CN}$  and  $2 \text{H}_2\text{C}=\text{N}-\text{NO}_2$ . The MRDX branch of the reaction can decompose to form  $\text{H}_2\text{C}=\text{N}-\text{NO}$  and  $2 \text{H}_2\text{C}=\text{N}-\text{NO}_2$ . These decomposition reactions involve breakage of the N-C bonds in the RDX ring structure, a common mechanism proposed for the pyrolysis of nitramines.

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<sup>1</sup>R.A. Fifer, S.A. Liebman, P.J. Duff, K.D. Fickie, and M.A. Schroeder, "Thermal Degradation Mechanisms of Nitramine Propellants", Proceedings of the 22nd JANNAF Combustion Meeting, CPIA Publication 432, Vol. II, October, 1985.

In addition, the authors of Reference 1 point out that other possible reactions may exist, such as: bimolecular or autocatalytic attack by reaction products (such as  $\text{NO}_2$ ), or intermediate radicals, on nitro oxygens or the C-H bond of unreacted RDX. This was rationalized by the apparent acceleration of the thermal decomposition of RDX in air relative to helium, which may be due to the reaction of  $\text{O}_2$  with NO to give additional  $\text{NO}_2$  which is then available to react with undecomposed RDX molecules.

Another study<sup>2</sup> by the BRL looked at the heat release from a LOVA propellant formulation (the same formulation as XM39, but with a unimodal RDX particle size distribution, 5  $\mu\text{m}$  avg.) when contacted with a hot metallic surface at atmospheric pressure. This was undertaken in an effort to better understand the mechanism for hot-fragment ignition (HFCIT) of LOVA propellants, but the results are also applicable to conductive ignition from an igniter source. The results given in that report indicate that a two-step sequence of global reactions exist, where the products of an endothermic reaction are the reactants in an exothermic reaction. The exotherm was described by the Arrhenius relationship, with the pre-exponential factor being a function of the heating rate.

A possible scenario for the thermal decomposition of RDX is one in which different rate-limiting reactions dominate, depending on the energy level of the combustion environment. In other words, during the ignition event, the thermal decomposition (pyrolysis) of the propellant, and specifically a single reaction in the decomposition process may control the rate at which the propellant ultimately burns. At higher temperatures and pressures, sufficient energy and reaction species are present to accelerate the rate of this reaction, thereby speeding the overall rate of reaction. As a result, a different rate-limiting reaction step may appear. If this scenario is accurate, then it is possible to accelerate the combustion rate by introducing reactive species (such as oxygen, or oxidizing agents) thereby increasing the energy level of the reactants by the release of energy from the primarily exothermic reactions. The rate limiting step may indeed be an endothermic reaction, however, such as the cleavage of bonds by pyrolysis or the phase change of a reactant. If this is the case, then an energy source is required, either from an igniter or exothermic propellant reactions, to produce acceleration of the overall combustion rate.

In addition to the chemistry requirement, a successful igniter material must also produce combustion products which are present in both gaseous and condensed phases. This ensures that the appropriate heat transfer to the propellant occurs over the temperature range. Igniters for all propellant types benefit from this characteristic; witness the popularity of black powder as an igniter material through the years. Condensed phase igniter products produce effective ignitions (even at the low

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<sup>2</sup>M.S. Miller, A.J. Kotlar, A. Cohen, D.L. Puckett, H.E. Holmes, and K. Troung, "Effective Ignition Kinetics for LOVA Propellant", BRL Memorandum Report, BRL-MR-3724, December, 1988.

temperature extreme) by transferring their heat content by conduction, directly to the propellant grains. However, an overabundance of heat transferred to the propellant grains by condensed phase products can cause an over-ignition of the propellant, leading to pressure waves, grain breakage and over-pressures. The gaseous igniter products transfer their heat content primarily by convective means. This is an inherently slower process and can be negatively affected by cooling at the low temperature extreme. Good ignition of any gun propellant is indicated by a relatively rapid, yet gentle, chamber pressurization. If the pressurization is too slow, the propellant is under-ignited, possibly leading to hang-fires or overpressures-- if ignition finally does occur. If the pressurization is too rapid, the propellant is over-ignited, possibly leading to pressure waves within the propellant bed, and over-pressures if propellant grain breakage occurs.

The task of igniting LOVA propellants then requires a trade-off between the chemical and energy (heat) requirements, as well as the phase distribution of the combustion products of the igniters. An incorrect balance of these criteria can result in under-ignited or over-ignited conditions. The phase distribution of the igniter combustion products can affect the energy density of the material contacting the propellant surface. For instance, a cooler igniter which produces substantial condensed phase products (such as black powder, flame temperature 2000 K) can actually bring more heat to bear on the propellant surface than a double based propellant igniter (flame temperature 3700 K), due to the large thermal mass of the condensed phase fraction. For LOVA applications, however, the higher temperature products may be required to accelerate RDX decomposition reactions.

The rheology of current LOVA propellants is such that, if ignited incorrectly, they are extremely sensitive to grain breakup at both ambient and low temperature levels. At the high temperature extreme, it has been found that some LOVA propellants are prone to agglomerate, possibly leading to lower than expected pressure levels, due to a decreased propellant surface area available for combustion.

## **Ib. SUMMARY OF RESULTS**

The experimental and analytical program described in this report represents a comprehensive effort covering many aspects of the igniter-propellant (LOVA) interactions. A technique for designing, fabricating and evaluating booster formulations for use in igniting a LOVA propellant formulation is presented. The evaluation of the booster materials includes measurement of the relative heat and pressure outputs, the efficacy of propellant ignition, and the effect on propellant combustion chemistry. In addition, a gas sampling technique for evaluation of the combustion gas chemistry is presented and

evaluated at a range of pressure levels. The results obtained are quite good and indicate that this technique may be a promising method for development and evaluation of booster materials for LOVA propellant ignition. While additional work is clearly needed, this program has provided a large step toward refining this technique into a viable and useful diagnostic tool.

**Table 1. Summary of Results From Igniter Development Studies**

### **PROPRIETARY INFORMATION**

The NASA-LEWIS thermochemical code was utilized to obtain a booster formulation (Mix 1) with a maximum theoretical oxygen output for use in igniting LOVA propellants. Three other booster materials were formulated to produce a slate of materials with a broad range of output properties. The experimental techniques developed, when combined with judicious use of thermochemical calculations using a theoretical computer code, resulted in the development of two promising LOVA propellant igniter

**CONFIDENTIAL PROPRIETARY INFORMATION:** *Information in Table 1. is subject to the restriction on the cover page of this report.*

materials. The results of the specific experimental test series are outlined in the remainder of this section, and summarized in Tables 1 and 2.

The tests conducted to evaluate igniter materials using the calorimeter provided a thorough understanding of the properties of the four booster mixes investigated, but little insight into which would serve as the best LOVA propellant igniter material. The compositions of the various booster mixes (denoted Mix 1 through 4) are defined above in Table 1. Mix 3 produced the greatest heat output, as well as the largest (theoretical) condensed phase fraction, but the smallest free oxygen output. The experimental heat results for Mixes 2 and 4 were inconclusive, although theoretical calculations predict that Mix 4 should produce the greater output. In a subsequent section, however, an argument is presented which suggests that incomplete combustion may have occurred during the three-pellet, Mix 4 test and that, according to theory, the heat content of Mix 4 does surpass that of Mix 2. Mix 4 produced the second largest condensed phase fraction and twice as much free oxygen as Mix 3. Mix 2 produced the smallest condensed phase fraction and, by inference, the largest gaseous phase fraction, evidenced by the largest pressure output. In addition, Mix 2 produced the second largest free oxygen output, as predicted by the NASA-LEWIS code. This is interesting since Mix 2 also contains the largest nitrocellulose content, which is known to consume available free oxygen as it burns. Evidently, the inclusion of the perchlorate more than made up for the oxygen debt incurred by the high nitrocellulose composition. Mix 1 produced the smallest heat output, but relatively high condensed phase fraction and the highest fraction of free oxygen. In addition, Mix 1 clearly demonstrated a more reactive chemistry, evidenced by a chemical attack on the copper of the calorimeter. The results of effectiveness testing of each of these booster mixtures in igniting the HELP1 LOVA formulation are discussed below. This information is necessary in order to establish the relative contribution of the different booster outputs (i.e. heat, condensed phase and oxygen) to ignition of LOVA propellants.

The results of the ignition effectiveness tests shed some light on the effect of the various igniter characteristics (i.e. heat, condensed phase and oxygen) on the ignition of LOVA propellant. These data are also summarized in Table 1, indicated by the average ignition time values. The level of reproducibility, then, is represented by the standard deviation of the ignition time. The booster mix which produced the greatest heat and condensed phase outputs (Mix 3) exhibited the shortest, yet one of the most irreproducible, ignition times. In addition, the booster mix which produced somewhat reduced heat and condensed phase outputs, but somewhat higher free oxygen output (Mix 4), exhibited very irreproducible results with the large grain propellant, yet quite good results with the small grain propellant. This could indicate marginal ignition functionality, or the need for more exhaustive experimental testing to obtain more statistically meaningful data sample sizes. The results for each of the remaining booster mixes (Mixes 1 and 2) were superior to both Mix 3 and 4 for both the large and

small grain experiments. Mix 2 produced excellent results for both propellant granulations, showing better overall reproducibility and somewhat shorter ignition times than Mix 1. These results do not suggest any functional dependence of ignition on the generation of condensed phase products, since Mix 2 produces the smallest fraction of this material. This may indicate that a threshold requirement exists for condensed material, above which no effect is realized. This does not suggest what might occur at reduced temperature levels, however, where condensed phase output has been shown to be beneficial to achieving good LOVA propellant ignition. In addition, it appears as if the booster producing the highest heat output (Mix 3) achieves the least overall reproducible ignitions, suggesting that this material is lacking in some key ingredient, such as oxygen. Conversely, the booster producing the highest free oxygen outputs (Mix 1) output produces acceptable ignitions, but with longer ignition times and slightly less reproducibility than a mix which sacrifices some free oxygen output for more heat and gaseous product generation (Mix 2). Clearly the production of sufficient oxygen, as well as heat are necessary for achieving good, reproducible, LOVA ignition.

There appears to be a rough correlation between the relative ignition times observed for each booster material and the heat outputs for each. The results for both the large and small grain tests show Mix 3 to have the shortest ignition time, Mixes 2 and 4 to have quite similar ignition times, and Mix 1 to have the longest ignition time. This ranking is quite similar to that resulting from the calorimeter heat study. This evidence supports the kinetic effect mentioned in the Introduction, where an endothermic reaction described by the Arrhenius equation gives way to the exothermic combustion reactions, once the propellant has been ignited. In this instance, the increased heat acts to accelerate the rate of the endothermic rate-limiting reaction. However, the acceleration effect appears to have greater variability if sufficient oxygen generation does not also exist. This could indicate that the oxygen acts to further accelerate combustion reactions, so that the continuation of the ignition depends more on heat generated by combustion and less on heat generated by the igniter.

**Table 2. Summary of Results From Combustion Gas Sampling Analyses**

Ignition source	Grain size	Pressure (psi)	CO/CO <sub>2</sub>	CO/N <sub>2</sub>	H <sub>2</sub> /N <sub>2</sub>	CH <sub>4</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>
Hot-wire	small	358	2.51	1.24	0.0490	0.0183	0.495
Igniter Mix 1	small	346	0.231	0.262	N/A	.00132	1.13
NASA-LEWIS (No Air)	—	340.1	6.925	1.579	0.0662	2.18 E-8	0.228
NASA-LEWIS (With Air)	—	306.4	2.113	0.544	0.0135	1.59 E-10	0.257

The combustion gas sampling results show reasonably good agreement with theoretical predictions obtained using the NASA-LEWIS code. These results are shown in Section II, Figures 12 through 16, and summarized in Table 2 for a given pressure. The similarity of the experimental values with the theoretical was not anticipated. Due to the nature of the combustion environment during ignition (especially by hot-wire), the experimental results were expected to deviate substantially from equilibrium calculations. However, major deviations from theoretical values are only present in excess amounts of both  $\text{CO}_2$  and  $\text{CH}_4$ , indicated by the  $\text{CO}_2/\text{N}_2$  and  $\text{CH}_4/\text{N}_2$  ratios in Table 2. Table 2 also shows the importance of atmospheric oxygen to combustion at low pressures. Two theoretical data sets are presented, one which utilizes an atmosphere of air in the combustion calculations, and one which ignores the contribution of air completely. As the table indicates, a substantial difference in the resulting product ratios is obtained by the introduction of air to the calculation. Comparisons of these theoretical values as a function of pressure are presented in Section II, Figures 12 through 16.

The large excess of  $\text{CO}_2$  was not expected, since incomplete (non-equilibrium) combustion is typically results in larger CO concentrations. However, the considerable magnitude of the methane ( $\text{CH}_4$ ) concentration does indicate a deviation from equilibrium calculations. The experimental methane ratio (Figure 16) was orders of magnitude (a factor of about  $10^5$ ) greater than equilibrium predictions. This is the strongest evidence for non-equilibrium or pyrolysis reactions. Large concentrations of methane (along with hydrogen) are expected during pyrolysis or incomplete combustion (oxidation).

The results obtained for the combustion gas sampling analyses underscore the importance of oxygen in the ignition of a LOVA propellant formulation (HELP1). A promising igniter, which produced a large quantity of free oxygen, was utilized to ignite a bed of HELP1 propellant in a gas sampling test. The results, when analyzed, indicated a more oxygen-rich ignition environment. In addition, the product ratios of interest tended toward the direction of the equilibrium values (i.e. more  $\text{CO}_2$  and less CO as well as reduced  $\text{CH}_3$  and  $\text{H}_2$  production), when this igniter was utilized.

## 1c. CONCLUSIONS

As a result of this program, several conclusions may be drawn. First and foremost, the testing procedures developed provide a comprehensive scheme which can be utilized to develop promising LOVA igniter materials. The various aspects of the analytical program include:

- Booster design and evaluation using the NASA-LEWIS thermochemical code;
- Booster pellet fabrication techniques;

- Booster testing using a calorimeter arrangement in a closed bomb;
- Booster ignition efficiency using a closed bomb loaded with LOVA propellant;
- LOVA combustion gas evaluation using a vented bomb and gas sampling hardware;
- Combustion gas analysis using gas chromatography.

Results from the various phases of the development program indicate:

- Ignition time appears to be directly proportional to the measured heat output, and theoretical temperature, of a slate of booster materials;
- Good, reproducible LOVA ignition requires substantial oxygen generation in addition to the heat requirement;
- Little sensitivity to condensed phase concentration was observed within the range of parameters investigated during this program;
- Booster materials which generate a great deal of free oxygen drive the LOVA combustion product ratios toward equilibrium;
- Two promising booster materials (Mixes 1 and 2) were identified which produced acceptable ignition characteristics for each of two different granulations of the HELP1 LOVA propellant formulation.

## Section II

### IIa. EXPERIMENTAL APPARATUS AND TECHNIQUES

#### *Experimental Hardware*

An existing closed bomb (50 cc) was utilized for each of the different types of experiments conducted during the present effort. To perform some of the special diagnostic testing required by this program, two special endcaps were fabricated for use with the bomb. One of the endcaps was designed to accept an M115-type primer and igniter flashtube. In this way, propellant can be ignited within the bomb using an ignition system similar to that for a 25mm cannon. This endcap was also adapted so that an electric initiation system could be used to ignite propellant utilizing a "hot-wire". The other endcap contains a port (0.5 in. or 12.7 mm diameter), to which a rupture disk holder and gas sampling apparatus is mounted. This was designed to allow the gaseous products of propellant combustion to be collected with a sampling vessel after the combustion event was interrupted at various burst pressure levels. The closed bomb and gas sampling configuration (using hot-wire ignition) is shown schematically in Figure 1. With the bomb configured in this way, the total volume of the system was increased to 68 cc.

In addition to the endcaps, a calorimeter was fabricated from copper (11200 and 12200 alloys). The calorimeter assembly consists of a cylinder (1.230 in. O.D., 0.980 in. I.D. and 2.150 in. long) with two end plates (0.125 in. thick). The calorimeter was designed to fit inside the closed bomb, and has a total mass of 171.2 grams. A Teflon sheet 0.030 in. thick was utilized to insulate the calorimeter from the closed bomb. A type K thermocouple was attached to the center of the calorimeter to measure the steady state temperature rise associated with each igniter tested. Using this measurement in conjunction with equation (1), defined in a later section, the total heat absorbed by the calorimeter was determined for each booster formulation. The heat output per unit mass for each booster formulation was then determined by subtracting the primer contribution and dividing by the booster mass. The calorimeter contains two small holes in the sidewall of the cylinder, one to allow pressure measurement and another to allow for release of combustion gases after a test.

A gas sampling apparatus was constructed to permit the analysis of propellant combustion gases. This device is also depicted in Figure 1, and consists of the closed bomb and special endcap

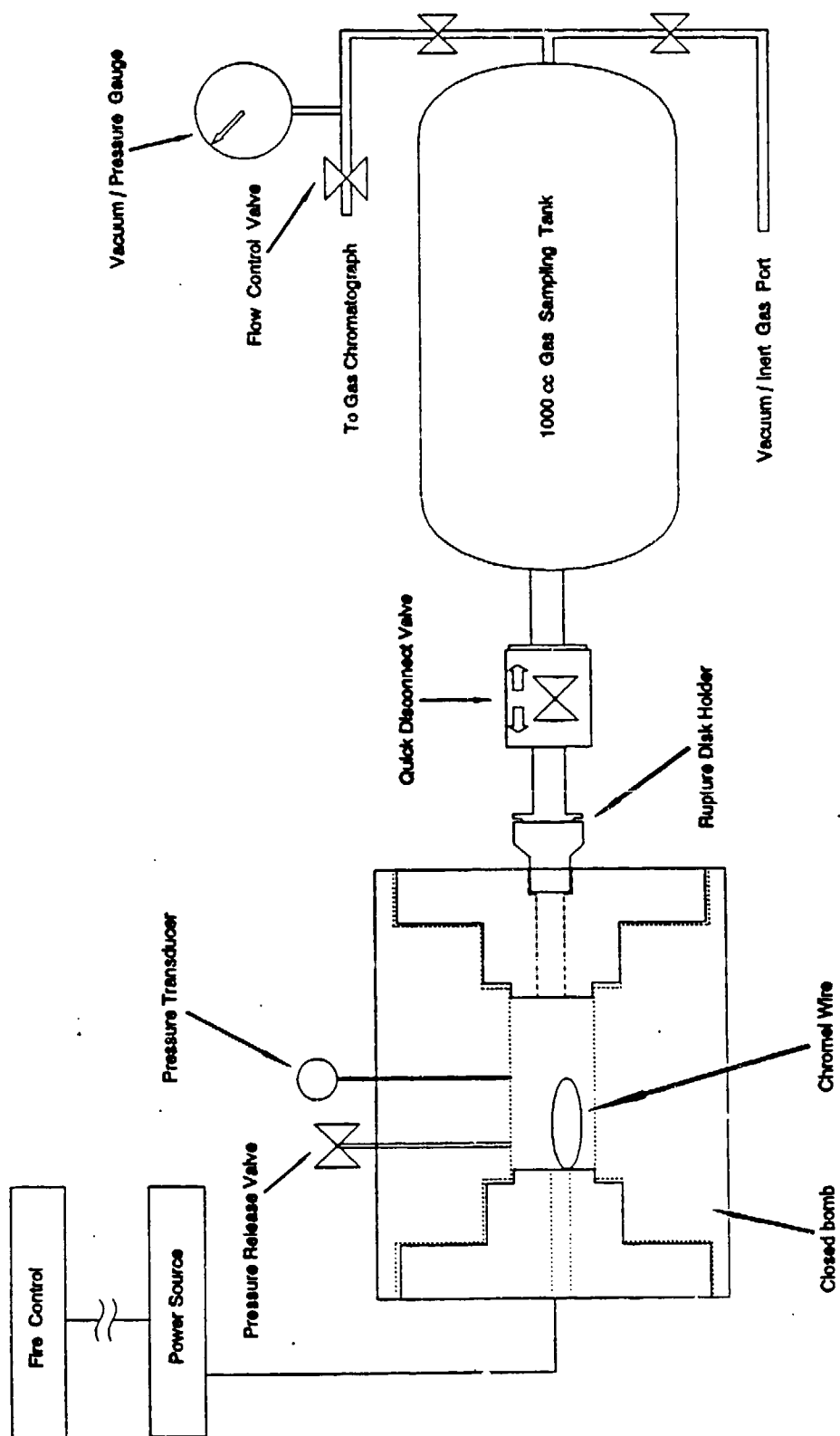


Figure 1- Schematic of Gas Sampling Apparatus.

described above, a rupture disk holder, quick disconnect valve, a 1000 cc sampling tank and various valves, fittings and gauges. The design of the apparatus is such that after a closed bomb test is performed, the gas sampling system can be removed at the quick disconnect valve, brought to the laboratory and connected to the gas chromatograph for determination of the gas composition.

For all of the closed bomb experiments, the pressure and temperature data were obtained using Nicolet 2094 digital storage oscilloscopes, and stored on floppy disks. The data were then reduced using IBM PC-compatible computers with the VU-POINT<sup>\*</sup> software package. All pressure data were obtained using PCB model 119A ballistic piezoelectric pressure transducers. For the chemical analysis, a Perkin-Elmer model 8500 gas chromatograph with intelligent data interface was utilized. With this interface, the GC data could be stored on a dedicated IBM PC-compatible computer for analysis or re-analysis at any time.

#### *Propellant Formulations*

Two granulations of the HELP1 propellant formulation were used in this study. In many of the tables and plots in this report references are made to "small grain" and "large grain" propellant. Small grain refers to a seven-perforation granular propellant with an outside diameter of 0.114 inches, a length of 0.244 inches and an average web of 0.025 inches. Large grain (also referred to as XM43) refers to a seven-perforation granular propellant with an outside diameter of 0.323 inches, a length of 0.562 inches and a web of 0.052 inches.

#### *Gas Chromatography*

As mentioned above, a Perkin-Elmer model 8500 gas chromatograph was utilized to determine the quantity of various permanent gases in the gas mixtures obtained from combustion of samples of the HELP1 propellant formulation. A ten (10) port gas sampling valve was utilized to inject constant volume (0.1 cc) samples of a gas mixture onto the separative columns for analysis. A thermal conductivity detector was used to quantify the component compositions. Two GC columns were necessary to achieve the desired gas separations. These were, namely, a 0.125 in. diameter, 6 ft. long Chromasorb 102 column (60/80 mesh) and a 0.125 in. diameter, 6 ft. long 5 Å molecular sieve (also 60/80 mesh).

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<sup>\*</sup> VU-POINT is a product of S-Cubed, a division of Maxwell Laboratories, Inc.

Two separation columns were required for this analysis since no single column could be found which had the ability to properly separate the five gases of interest. These gases are: CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. The molecular sieve column has the ability to separate all of these gases except for CO<sub>2</sub>, which becomes adsorbed onto the column packing. The CO<sub>2</sub> can only be removed from the column by exposing it to elevated temperature (250 °C) for a period of time. Even then, there is some question as to whether all of the CO<sub>2</sub> has been liberated, since the adsorption-desorption mechanism is a kinetic event following the Langmuir adsorption model. In any event, a superior analytical procedure was utilized to determine the CO<sub>2</sub> concentration, and is outlined below.

The approach utilized for the separation and analysis of CO<sub>2</sub> by gas chromatograph, was column sequence reversal. This technique utilizes two columns in series, in this case the chromosorb and molecular sieve columns, respectively. The chromosorb column was utilized to slow down and thereby separate the problem gas (CO<sub>2</sub>) from the remainder of the gas mixture. The order of the columns was then switched (via the ten-port valve) after all of the gases (except for CO<sub>2</sub>) exited the first column. In this way, when the CO<sub>2</sub> exited the chromosorb column it was sent directly to the thermal conductivity detector, never having seen the molecular sieve column. Other species, depending on their respective retention times in the molecular sieve, may have passed through two or three columns (i.e. the chromosorb twice). Needless to say, timing was critical to obtaining useful results using this analytical technique.

The combustion gas mixtures analyzed contain a great many constituents, as shown later in Figure 17. Only five of these gases were quantified during the present study. It was crucial, then, for the identity of each gas to be determined without question. To accomplish this, gas standards were obtained and calibration factors determined for each species. The retention times determined for each species during calibration runs (pure gas

component) did not match exactly the retention times of the suspected species in the combustion gas mixture. This is a common occurrence, since gas-gas interactions can inhibit or accelerate the flow of specific gas species through a chromatographic column. However, to clarify the situation, calibration by

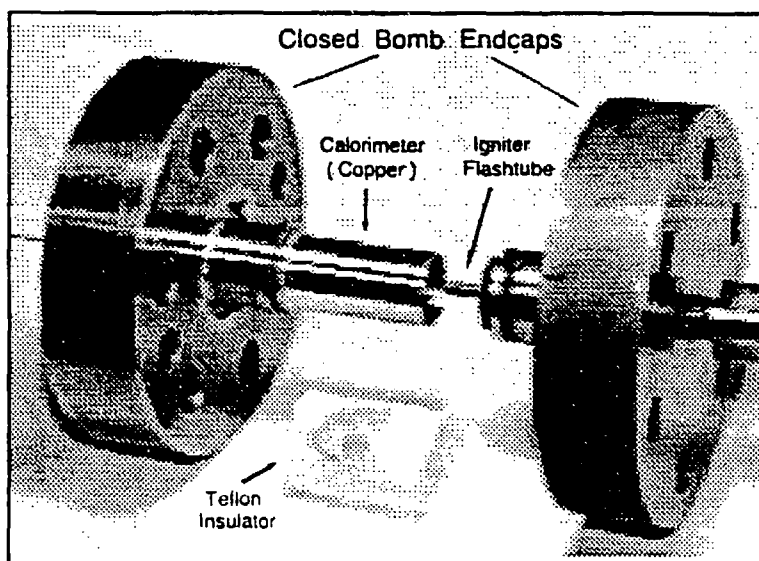


Figure 2- Videograph of Closed Bomb Calorimeter Configuration.

internal standard was performed to positively identify the peaks of interest. A combustion gas sample was obtained, using a technique outlined later in this report, and a chromatographic analysis performed. An amount of one of the standard gases was then added to the gas sample and the mix re-analyzed at the same pressure. Ratios of the two analyses were calculated with the computer; the peak showing a large (factor of 2 or 3) increase in area was identified as the standard gas. This was repeated for each gas of interest to positively determine the retention times of each species.

### *Calorimeter Test Series*

As mentioned earlier, an experimental test series was conducted to evaluate various igniter materials. For this testing, a calorimeter was utilized to obtain the heat output per unit mass of booster material. The experimental configuration used is depicted in Figure 2. In addition, the gas pressure was recorded to obtain a measure of the relative impetus from the gaseous products produced by each formulation. The primers utilized for this testing were of the M115-type (25mm cannon primers). However, instead of the standard FA956 mix, these contained 0.180 grams of the OMark 308 mix. This primer has been found to provide a good ignition interface for LOVA propellants, when teamed with an appropriate booster material, partially due to its lower brisance.

After several preliminary tests were conducted with different flashtube lengths and hole patterns, a final experimental configuration was determined which utilized a one-inch long flashtube with eight radial holes (0.078 in. diameter) and one axial hole (0.125 in. diameter). This flashtube geometry is pictured in

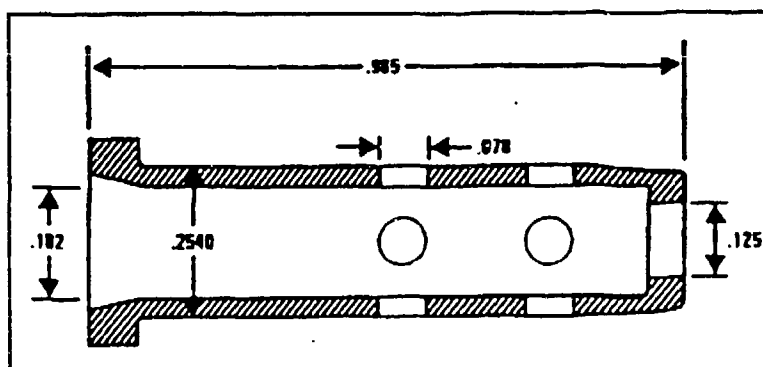


Figure 3- Schematic of Flashtube Geometry.

Figure 3. Once defined, this geometry was utilized for virtually all tests which required a primer/booster igniter. For each of these tests, the booster material was placed in close proximity to the primer prior to testing. This configuration was established as a result of earlier tests which utilized a longer flashtube (1.5 inches) with the booster pellets away from the primer. Observations made following these tests indicated that little or no booster combustion occurred during the test. This was attributed to the fact that much of the primer gas had vented or cooled prior to contacting the booster material. It was, therefore, shown that the location of the booster material within the flashtube is critical if all of the benefits of a given booster mix are to be realized. This fact may have been overlooked had the igniter

been tested in a gun, since the booster would most certainly have been consumed during the course of the combustion cycle.

### *Ignition Effectiveness Test Series*

An experimental test series was also conducted to evaluate the ability of the various booster materials to ignite the two HELP1 granulations. These propellants were loaded into the closed bomb at a density of approximately 0.1 g/cc. This test series utilized the same hardware configuration mentioned above, with the exception that the calorimeter was not used. The objective of this series was to measure the pressure in the closed bomb as a function of time and determine the ignition time and action time for a given test. In these tests, the ignition time is defined as the time from the onset of pressurization, to the time when a rapid change in pressure is experienced. This change in pressure is indicative of self-sustained propellant combustion, thereby signifying the end of the ignition event. Action time is defined as the time from the onset of chamber pressurization to the time of peak chamber pressure.

### *Combustion Gas Sampling Tests*

Evaluation of propellant combustion gas products was performed using the experimental configuration depicted in Figure 1. For almost all of the testing conducted in this way, hot-wire ignition was utilized. A chromel wire, typically 2.5 in. in length, with a 0.020 in. diameter and powered by a six volt, low-current, DC power source, was used to ignite the propellant. The objective of this experimental series was to determine the combustion gas product ratios of the two propellant granulations at various pressure levels. These values were then compared to equilibrium values determined using the NASA-LEWIS thermochemical code. The pressure level at which the combustion gases were obtained was determined by the appropriate choice of a rupture disk. The rupture disks and stainless steel holder were produced by Fike Metal Products Corp.

Prior to conducting a test, the sample tank and associated plumbing were evacuated and filled with one atmosphere of helium. Helium was chosen instead of air since it is not a participant (inert) in the combustion reactions (oxygen is a reactant and nitrogen a product of the combustion reactions). In addition, it is the carrier gas utilized in the gas chromatograph and therefore does not appear in the gas analysis. The sampling system was then attached to the closed bomb via the quick disconnect valve. The design of this valve is such that when disconnected, both ends of the system are sealed. No

attempt was made to evacuate the closed bomb or the region between the rupture disk and the quick disconnect. This allowed a small volume of air to be present during the combustion. As will be seen in a later section, this small air volume can have a significant effect on the equilibrium combustion products at low pressures.

The propellant loading density for these tests was 0.073 g/cc, with a propellant mass of approximately five (5) grams and a bomb volume of 68cc, when used in this configuration. Some early testing utilized approximately ten (10) grams of propellant; however, difficulties (possibly unrelated) were encountered when trying to quench these samples. In any event, five (5) gram loads were utilized for virtually all of the gas sampling tests. In order to achieve good contact between the hot-wire and the propellant, the wire loop was run through the perforations of one or more propellant grains prior to testing. For the large grain (XM43) tests, the wire was looped through two perforations of a single grain, while for the small grain tests, the wire was looped through a single perforation of three propellant grains. For these tests, the chamber pressure was the only data recorded. This data was utilized to, among other things, obtain the actual pressure at which the combustion event was interrupted or vented.

Difficulties were encountered during the determination of the hot-wire experimental configuration. Initially, tungsten wire was utilized with a much stronger 12 VDC power source. This combination provided an ignition so strong that it was virtually impossible to quench. This was probably due to the fact that the hot-wire continued to ignite propellant after the time when the rupture disk failed. The weaker power source and chromel wire configuration ultimately settled upon, provides a strong heat source for a finite period of time. The heat from the power source is sufficient to cause this wire to fail, thereby terminating the ignition event. In fact, nichrome wire was also tested with this same power source and proved too weak to maintain its integrity long enough to ignite the propellant at all. Therefore, it is critical that the power source and wire material are matched properly to achieve an acceptable ignition event, when igniting LOVA propellants with a hot-wire.

After a combustion gas sample was collected in the sampling apparatus, sufficient time was allowed for the gases to cool (ten to fifteen minutes) before removing the sample for analysis. In this way, the probability of high-pressure noxious gases existing within the sampling apparatus was minimized. It should be noted that the pressure within the sampling apparatus was monitored using the attached pressure gauge, ensuring a safe pressure level before the tank was disconnected. The sampling tank was then removed via the quick disconnect and connected to a ten (10) port gas sampling valve, located on the gas chromatograph. Chromatograms of the gas mixture were then obtained and either analyzed immediately, or stored for later analysis on the dedicated computer

system. The relative masses of the permanent gas species of interest, namely: CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>, were determined from the analysis. These gases were selected to give a representative picture of the state of combustion equilibrium, with minimum risk to the investigators. Other gases which may be used to evaluate non-equilibrium conditions (NO, NO<sub>2</sub> and HCN) are extremely toxic. The handling of these materials to calibrate the chromatograph was deemed too hazardous at this stage of the program.

The GC analyses of the combustion gas products were conducted at relatively low sample injection pressures (less than 5 psig), which were not necessarily equal to the pressure in the sample vessel. In order to normalize the results, mass ratios of component species were generated for comparison to theoretical values obtained from NASA-LEWIS code calculations. The component ratios utilized for these comparisons were: CO/CO<sub>2</sub>, CO/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, and CH<sub>4</sub>/N<sub>2</sub>.

In addition to the tests using ignition by the hot-wire arrangement, a single combustion gas sampling test was conducted using the primer/booster ignition configuration, similar to that used in the calorimeter and ignition effectiveness tests described earlier. The flashtube utilized in this test was longer (1.5 inches), yet still contained the same number of radial vent holes (8) as the shorter tube. This tube did not contain an axial vent hole, however, so that no pressure could vent from the end of the flashtube to prematurely burst the rupture disk. The objective of this test was to determine the effect of a promising igniter system on the combustion gas product ratios determined using hot-wire ignition. For the test, two pellets of Mix 1 (defined below) were combined with the OMark 308 primer. In addition, a slightly larger mass of the small grain propellant was loaded into the bomb (6.2 grams), to more closely match the loading density used in the ignition effectiveness testing.

## IIb. EXPERIMENTAL RESULTS AND DISCUSSION

### *Igniter Material*

Based on the general requirements for a good LOVA igniter, presented in Section I, various potential ingredients for incorporation into booster materials were identified. A great many mixtures of these ingredients were defined and thermochemical outputs calculated using the NASA-LEWIS code. The various components and mixtures which can be identified are practically limitless, however, a great many of these potential candidates were eliminated by evaluation of the resulting thermochemical properties of these mixtures. The criteria utilized for determining possible candidates were essentially those discussed in the Introduction, namely: the quantity of free oxygen generated, the heat output of the products (temperature), and the fraction of condensed phase products produced. Prospective

booster formulations were removed from consideration if the combination of the oxygen output, temperature and condensed phase products were inferior to other formulations. The ranking used for selecting a mixture was in the order listed.

The resulting calculations identified Mix 1, shown below in Table 3, as a promising candidate for an igniter material. This material produced a greater quantity of free oxygen, a necessary ingredient for any LOVA igniter, than any of the other materials examined. This increased oxygen output came at a cost, however: a somewhat reduced flame temperature and a smaller condensed phase fraction than was available from other formulations. The results of thermochemical calculations, using the NASA-LEWIS code, for Mix 1 (as well as the other three mixes tested) are contained in the Appendix, and summarized in Table 4.

**Table 3. Composition of Booster Formulations (Weight Percent)**

### **PROPRIETARY INFORMATION**

The booster formulations listed in Table 3 were mixed and pressed into pellets. Both of these operations were done by hand. When mixing these materials, a minimal amount of acetone was utilized as a processing aid. The moist mixtures were stirred until dry, then ground using a mortar and pestle. Before pressing, the mix was moistened with acetone vapor to aid in adhesion. The final pellets were then dried at 60 °C for several hours to ensure that all of the solvent was removed. All of the igniter pellets fabricated in this way had good physical strength, with nominal dimensions of 0.167 in. outside diameter, 0.060 in. inside diameter, and lengths of 0.177 in. The resulting mass of the pellets was approximately 0.125 grams. The aluminum used in these mixtures was in the form of a very fine powder (Alcoa atomization grade 101, 17-24  $\mu\text{m}$  average particle diameter). The nitrocellulose was derived from a single-based propellant (M10) formulation with the generic name of CBI (clean-burning igniter).

The remaining three booster mixes listed in Table 3 represent parametric variations of a single component concentration, with the ratio of the remaining three held constant with respect to each other. Mix 2 has an increased nitrocellulose content, while the ratio of the other three constituents relative to

**CONFIDENTIAL PROPRIETARY INFORMATION:** *Information in Table 3. is subject to the restriction on the cover page of this report.*

each other is held constant. Completing the slate, Mix 3 has an increased aluminum content and Mix 4 a decreased potassium perchlorate content. This slate allows the effect of specific component species concentrations to be evaluated with respect to experimental parameters such as heat output and gas pressure. In addition, this slate of booster compositions provides a slate of igniter materials with a large range of output characteristics. With this, it should be possible to determine the relative importance of the evaluation criteria to LOVA ignition. In other words, of the free oxygen, heat output and condensed phase output, what combination produces the best igniter material?

**Table 4. Results of Thermochemical Calculations for Booster Formulations**

PARAMETER	Mix 1	Mix 2	Mix 3	Mix 4
Temperature (K)	2935.	3204.	4511.	3607.
Condensed Fraction (wt %)	22.70	13.49	33.29	29.68
Oxygen Fraction (wt %)	15.08	9.82	3.06	6.24

As the thermochemical results in Table 4 show, Mix 3 produces the largest condensed phase fraction and highest temperature products. However, this mix also produces the smallest free oxygen fraction of the four mixes. The free oxygen fractions listed in Table 4 represent a sum of both the O and O<sub>2</sub> contributions from the equilibrium calculations. Mixes 4 and 2 show gradual increases in the free oxygen content, with a corresponding decrease in both the temperature and condensed phase fraction. This corresponds to a decrease in the aluminum concentration and increase in the nitrocellulose concentration, as shown in Table 3. The results for Mix 1 in Table 4 indicate a moderate condensed phase fraction with by far the highest oxygen fraction. However, the resulting temperature for this mix was the lowest of the four. This discussion highlights the dependence of the booster output characteristics on the relative chemical compositions, as well as the interdependence of the output parameters. In other words, to increase the quantity of a specific output parameter, such as free oxygen, by modifying the composition, a sacrifice of another output parameter, in this case heat, will result. It should be possible, however, to determine an optimum balance between the specific output requirements, once they are determined, so that a single booster formulation with satisfactory output characteristics may be identified.

While it is recognized that all three of the parameters listed in Table 4 are important in achieving good LOVA ignition, the relative sensitivity of the ignition to these parameters is not clear. Mix 1 was selected as a candidate formulation since it produces what was believed to be acceptable levels of all elements of the three selection criteria. This mix also produced the largest free oxygen output of any formulation studied, however, it was not known at that time which of the three selection criteria was the most important for LOVA ignition. This can best be determined experimentally. Therefore, the other three booster mixes were formulated so that a comprehensive slate of booster materials, with widely varying chemistries and output characteristics, were available to help identify the sensitivity of LOVA propellant ignition to these parameters.

#### *Results of Calorimeter Experiments*

The results of evaluation tests using the calorimeter are given in Table 5 for igniter configurations using one, two and three booster pellets, respectively. The heat output was calculated using the maximum temperature change experienced by the calorimeter, utilizing equation (1) below. This equation was used to quantify the total heat transferred to the calorimeter from the booster material and primer. The heat output for each booster formulation was then obtained by subtracting the heat output associated with the primer (96.34 cal. or 535.2 cal/gram, a temperature rise of 6.08 °C), and normalizing the result by dividing by the mass of the booster tested.

$$\Delta H = mC_p\Delta T \quad (1)$$

where:  $\Delta H$  is the heat absorbed by the calorimeter;  
 $m$  is the mass of the calorimeter;  
 $C_p$  is the specific heat of copper;  
 $\Delta T$  is the change in temperature of the calorimeter.

As Table 5 shows, Mix 3 produces the largest and Mix 1 the smallest heat outputs for each test. The data for Mixes 2 and 4 do not clearly indicate which mix produces the larger heat output. For the one-pellet test, Mix 2 produces a higher heat output, while for the two-pellet test Mix 4 produces the higher output. The results for the three-pellet test were virtually identical, with Mix 2 producing a slightly higher output. The average values of the data in Table 5 were presented earlier in Section I, Table 1. As a result of this heat data alone, it is not possible to definitively say which (Mix 2 or 4) of these materials

produced the higher heat output. In subsequent discussion, however, an argument is presented which suggests that incomplete combustion may have occurred during the three-pellet, Mix 4 test and that, according to theory, the heat content of Mix 4 does surpass that of Mix 2.

One inch flashtubes were utilized to confine the booster materials for these tests. It was found that if the igniter pellets were not located near the primer initially, complete combustion may not result. During most of the testing, the pressure generated within the flashtube was sufficient to blow the end from the flashtube. In many tests utilizing two and three booster pellets, the end of the flashtube was literally blown apart, in a "banana peel" fashion. Therefore, discrepancies in the data for the two- and three-pellet tests may be related to whether or not the flashtube was destroyed during combustion of the booster material.

Table 5. Experimental Heat Output of Booster Mixes (Cal/gram)

Mix Number	Number of Igniter Pellets		
	1	2	3
Mix 1	716.7	732.3	781.6
Mix 2	806.7	890.4	858.1
Mix 3	1260.	1250.	1311.
Mix 4	733.7	952.5	853.6

The experimental heat results presented above (Table 5) are ranked similarly to the theoretical temperatures predicted by the NASA-LEWIS code, summarized in Table 4. Utilizing the temperature as an indication of the heat output, the predictions given in Table 4 indicate that Mix 3 will produce by far the largest, and Mix 1 the smallest, heat output; in agreement with experimental results. Table 4 also suggests that Mix 4 will produce a higher heat output than Mix 2. While the experimental results for the latter formulations were inconclusive, the two-pellet results do predict this ranking.

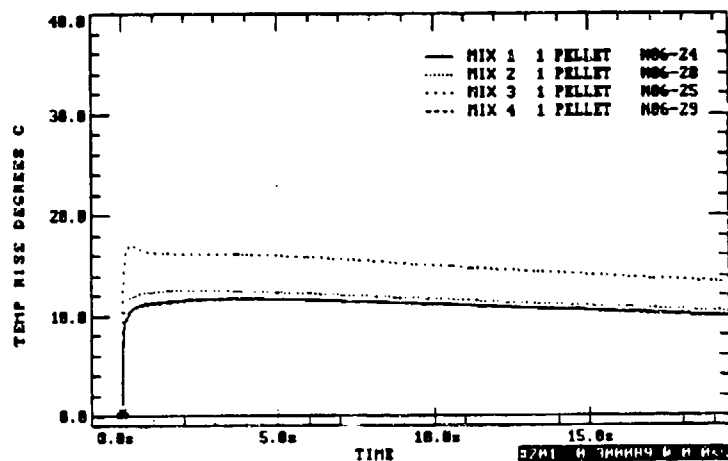


Figure 4- Calorimeter Data For One Booster Pellet.

The relationship between the heat output of a given booster formulation and its composition is not straightforward. As Tables 1 and 3 show, the booster formulation containing the highest aluminum content, as well as a high perchlorate concentration to provide oxygen (Mix 3), produced far and away the greatest heat output. However, the two formulations which produced the next largest heat outputs (Mixes 2 and 4) both contained relatively large nitrocellulose contents, but much less aluminum. Mix 1 produced the smallest heat output, yet did not have the smallest amount of any one ingredient. Indeed, this mix has the greatest concentration of potassium perchlorate. In this instance, heat production appears to have been sacrificed for the production of excess free oxygen. The heat output data resulting from the calorimeter tests (Table 5) give credibility to the accuracy of the remaining theoretical calculations summarized in Table 4.

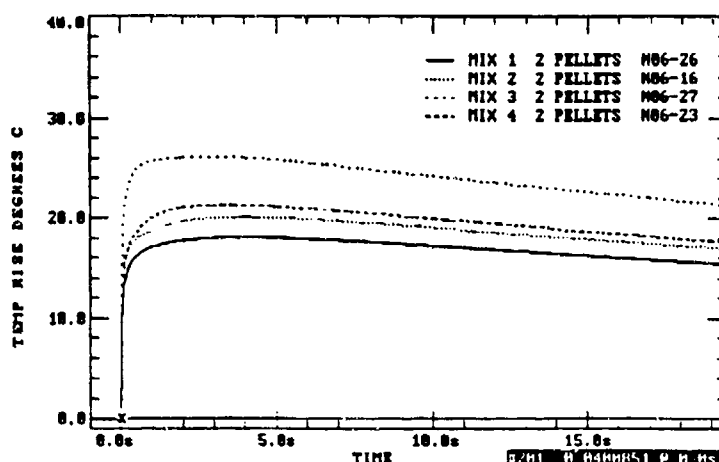


Figure 5- Calorimeter Data For Two Booster Pellets.

The calorimeter heat data are contained in Figures 4 through 6. Recall that the temperature rise in these figures represents the sum of both the booster and primer outputs. The temperature change used in Equation (1) is the steady state maximum temperature, measured at the plateau region after the steep rise in temperature histories shown in Figures 4 through 6. The

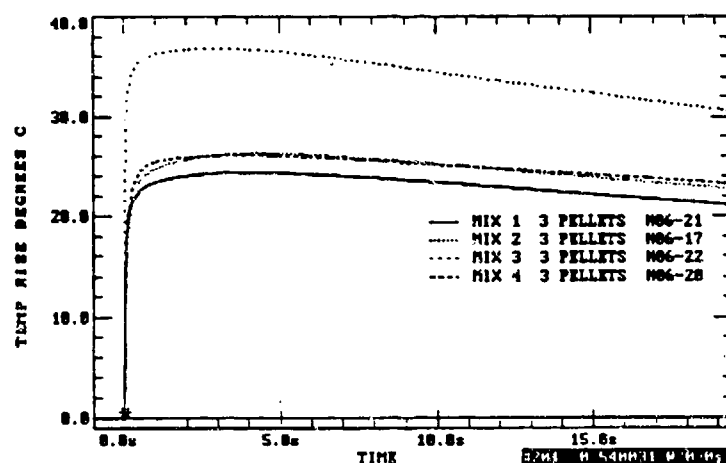


Figure 6- Calorimeter Data For Three Booster Pellets.

contribution of the primer to the measured heat was subtracted from each value to obtain the data in Table 5. Any unsteady effects, such as the peak seen for Mix 3 in Figure 4, are ignored. This effect was attributed to unsteady state heat conduction, possibly due to the deposition of hot condensed material near the thermocouple location.

The pressure data for the calorimeter test series is contained in Figures 7, 8 and 9, for one, two and three booster pellets, respectively. As the figures show, there are no large differences in the

pressure data for the slate of booster formulations, yet small differences are evident. First, as might be expected, Mix 2 produced the highest gas pressure in all cases. Mix 2 contains the highest nitrocellulose content, an energetic material which produces a high percentage of gaseous combustion products. The different booster formulations also seem to exhibit

differing burn rates. Mix 2 appears to burn the fastest in all cases, demonstrating the largest rate of pressure rise. This again appears to be attributable to the large nitrocellulose content, which has a rapid combustion rate due to its energetic nature. For the one-pellet tests (Figure 7), the remaining three mixes all burn at rates which are indistinguishable. A decrease in the slope of the pressure histories occurs for these formulations at about the 200 psi level. This pressure level is attributable to that developed by combustion of the primer. The more gentle pressure rise after this point, then, is attributable to the combustion of the respective booster formulations. A pressure trace showing the output from a primer alone is also given in each figure, and shows a slightly higher pressure (approximately 300 psi) than the 200 psi mentioned above. This is probably due to the fact that energy from the primer gases must be absorbed in igniting the booster pellets.

The two-pellet booster pressure data, shown in Figure 8, shows the same break in slope for two of the mixes (1 and 3), while Mixes 2 and 4 show a more rapid combustion with Mix 2 producing a slightly higher peak pressure. This trend correlates well with the nitrocellulose content of the boosters. Mixes 2 and 4 have much higher NC contents than do Mixes 1 and 3. The

slower-burning nature of the latter two mixes may lead to difficulty in igniting these formulations. It is unlikely that the mechanical properties of these booster formulations is responsible for the different burn rates observed. All of the formulations tested exhibited good strength characteristics. In fact, the

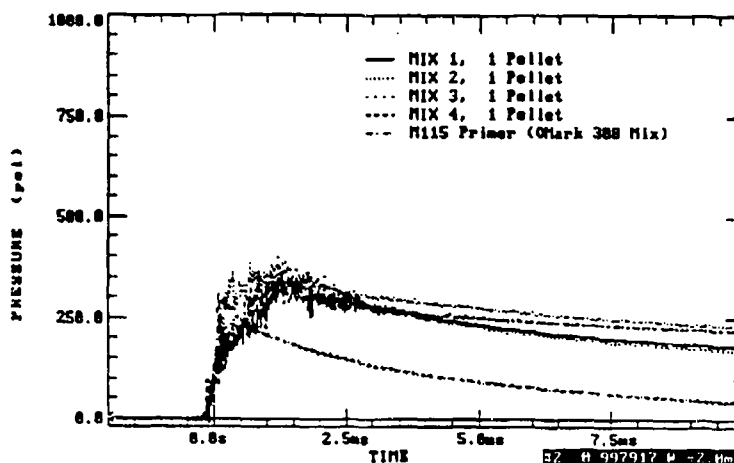


Figure 7- Pressure Data For One Booster Pellet.

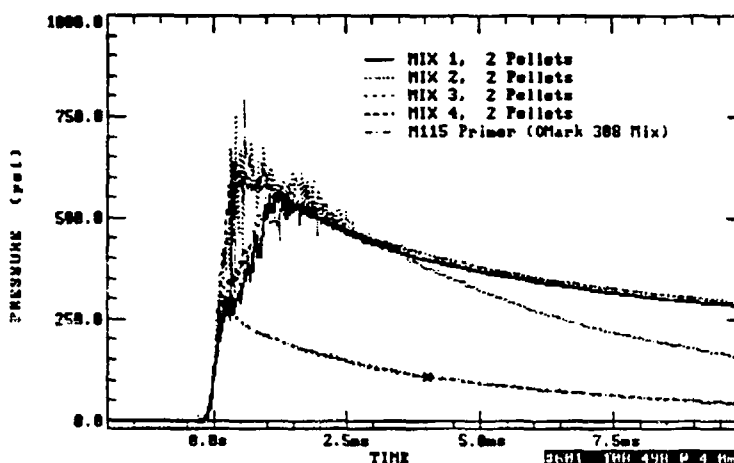


Figure 8- Pressure Data for Two Booster Pellets.

formulations which exhibit the fastest burning behavior also have the largest nitrocellulose content. In these formulations, nitrocellulose serves as an energetic binder. Consequently, the formulations with the largest binder content are expected to possess the strongest mechanical matrix.

The pressure data for the combustion of three booster pellets is given in Figure 9. The differences between three of the four mixes appear to be less than in the earlier tests. Mix 4, however, demonstrates a markedly lower pressure output than any of the other mixes. This does not track with the earlier testing and may be attributable to the fact that the one inch flashtube is virtually

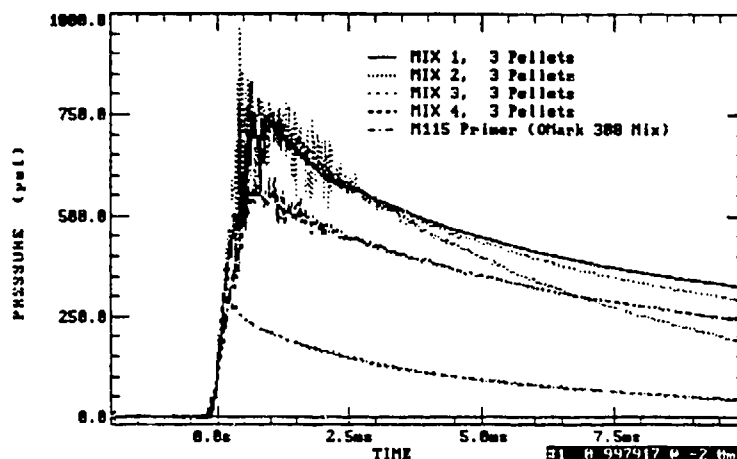


Figure 9- Pressure Data for Three Booster Pellets.

destroyed when testing three booster pellets. It is possible, then, that some of the Mix 4 pellets were blown from the flashtube and may not have been completely combusted. This speculation is strengthened by comparing the pressure level obtained for Mix 4 in Figure 9 (three pellets) with that in Figure 8 (two pellets). It can be seen that the observed pressure levels are virtually identical in the two figures. This also suggests an explanation for the lower-than-expected heat level for Mix 4 in the three-pellet configuration (Table 5), since theoretical calculations (Table 4) predict a higher heat output for Mix 4 than for Mix 2. Therefore, these unexpected variations may be related in some way to the integrity of the flashtube during testing.

A very interesting event occurred when more than one pellet of Mix 1 (formulated to have a high oxygen content) was burned in the calorimeter. After testing, the surface of the calorimeter was covered with a thick coating of a blue-green powder. A chemical analysis of this residue was not attempted, however, the material could possibly be a mixture of copper (II) hydroxide (blue), copper (II) chloride (blue-green) and/or copper (I) chloride (white). Whatever the identity of the reaction(s) with the copper, they did not occur with any other booster formulation. This suggests that the increased oxidative nature of the combustion products led to attack of the copper metal. This apparently only occurred when the heat output was sufficiently high, however, since this effect was not observed when only a single booster pellet of Mix 1 was tested.

The results of the igniter materials testing in the calorimeter give a more thorough understanding of the properties of the four booster mixes, but little insight into which material would serve as the best

LOVA propellant igniter material. Some general observations regarding the results of this testing are summarized here. Mix 3 produced the greatest heat output, as well as the largest (theoretical) condensed phase fraction, but the smallest free oxygen output. The experimental heat results for Mixes 2 and 4 were inconclusive, although theoretical calculations predict that Mix 4 should produce the greater output, and there is evidence that the three-pellet test may have produced erroneous results. Mix 4 produced the second largest condensed phase fraction and twice as much free oxygen than Mix 3. Mix 2 produced the smallest condensed phase fraction and, by inference, the largest gaseous phase fraction, evidenced by the largest pressure output. In addition, Mix 2 produced the second largest free oxygen output, as predicted by the NASA-LEWIS code. This is interesting, since Mix 2 also contains the largest nitrocellulose content, which is known to consume available free oxygen as it burns. Evidently, the inclusion of the perchlorate more than made up for the oxygen debt incurred by the high nitrocellulose composition. Mix 1 produced the smallest heat output, but relatively high condensed phase fraction and the highest fraction of free oxygen. In addition, Mix 1 clearly demonstrated a more reactive chemistry, evidenced by its attack on the copper of the calorimeter. The effectiveness of each of these varied mixtures in igniting the HELP1 LOVA formulation is evaluated in the next section. This information is necessary in order to establish the relative contribution of each category of the booster output (i.e. heat, condensed phase and oxygen) to ignition of LOVA propellants.

#### *Results of Ignition Effectiveness Testing*

The results of experiments to evaluate the ignition effectiveness of the set of booster materials are summarized in Table 6. These tests utilized a single pellet of the respective booster material along with the M115-type primer (0.180 grams of 308 mix), to ignite a bed of propellant in the closed bomb. The calorimeter was not utilized in this series of tests. The compositions of the booster materials were presented earlier in Table 3.

As stated previously, the Mix 1 formulation was selected as a result of calculations conducted to maximize the free oxygen output, without sacrificing greatly either the heat or condensed phase fraction produced. The remaining mixes were formulated by varying individual constituents while holding the ratio of the remaining components constant. In this way, a broad range of output characteristics were obtained from this slate of booster formulations. It is extremely difficult, if not impossible, to determine analytically which of the three igniter properties mentioned above have the greatest effect on propellant ignition. This is best determined experimentally, and serves as the objective for the phase of testing described in this section.

Table 6 gives data for ignition of both large (XM43) and small granulations of HELP1 propellant by each booster material, with two tests conducted for each booster and propellant combination. The measure of ignition effectiveness, tabulated for each test, are the ignition and action times. Ignition time is defined here as the time from the onset of chamber pressurization to the point where rapid chamber pressurization begins, which is indicative of self-sustaining propellant combustion and signifies the end of the ignition event. Action time is defined as the time from the onset of chamber pressurization to the time where peak chamber pressure occurs. The average values and standard deviations of the ignition time data were presented earlier in Section I, Table 1.

**Table 6. Summary of Ignition Effectiveness of Booster Materials**

Run Number	Propellant Granulation	Igniter Mix	Igniter Mass	Ignition Time (ms)	Action Time (ms)
N06-34	large	Mix 1	0.1279g	72.8	105.4
N06-35	large	Mix 1	0.1323g	70.1	102.1
N06-31	large	Mix 2	0.1240g	61.0	89.4
N06-36	large	Mix 2	0.1292g	61.8	92.0
N06-32	large	Mix 3	0.1230g	62.5	92.4
N06-37	large	Mix 3	0.1234g	53.7	80.5
N06-33	large	Mix 4	0.1236g	69.9	100.0
N06-38	large	Mix 4	0.1240g	54.8	84.0
N06-39	small	Mix 1	0.1244g	32.1	43.9
N06-40	small	Mix 1	0.1269g	32.2	44.0
N06-41	small	Mix 2	0.1232g	31.0	42.9
N06-42	small	Mix 2	0.1290g	31.1	41.8
N06-43	small	Mix 3	0.1219g	30.8	42.1
N06-44	small	Mix 3	0.1248g	29.6	42.0
N06-45	small	Mix 4	0.1229g	31.8	44.1
N06-46	small	Mix 4	0.1250g	31.7	43.3

The pressure data for these tests are shown in Figures 10 and 11 for the small and large grain propellants, respectively. Individual plots of the data for the various booster materials appear in the Appendix, Figures A1 through A10. In viewing the pressure data, it may be argued that the ignition

times listed in Table 6 appear somewhat arbitrary. However, these values were the result of careful data analysis. To determine the ignition time, the pressure data were differentiated with respect to time; the point in time where this differential experienced the onset of a rapid slope increase was identified as the ignition time. This technique appears reasonable, since pressure traces which appear similar produce similar ignition times using this method.

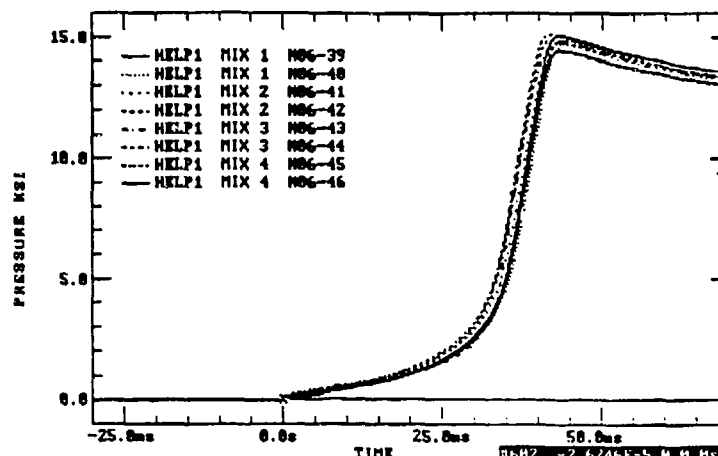


Figure 10- Pressure Data for Ignition of Small Grain HELP1 Propellant With Booster Mixes.

As is apparent from Figures 10 and 11, as well as Table 6, each booster mix is much more effective when igniting the small propellant granulation, showing shorter ignition times and better reproducibility than with the large granulation. The cause of this is attributable to the greater surface area of the small grains which allows more material to be ignited by a given igniter system. Once ignited, this provides increased burning surface area and resultingly larger gas generation rates, leading to shorter ignition times and faster flamespreading. In any event, the purpose of this testing was merely to evaluate the effectiveness of the igniter materials in igniting LOVA propellant, not to develop an ignition system for a specific propellant granulation. However, a successful igniter candidate should demonstrate superior ignition characteristics (short ignition times and good reproducibility) for both the large and small granulations. It should be noted, though, that due to the considerations mentioned above regarding surface area and gas generation rates, the ignition times of the large granulation will never be as short as with the small granulation, even when ignition effectiveness is comparable.

The results of testing with the small propellant granulation (Tables 1 and 6) show that three of the four booster mixes provide excellent ignition reproducibility (namely, Mixes 1, 2 and 4). Of the three, Mix 2 produced slightly shorter ignition times, while all three produced virtually identical action time reproducibility (Table 1). Mix 3 exhibited the poorest ignition reproducibility, yet had the shortest ignition times of the four mixtures, most likely as a result of the large heat and condensed phase outputs.

For the large granulation ignition tests, Mix 1 again performed quite well, and Mix 2 performed excellently, producing extremely reproducible (and short) ignition times. However, in contrast to the small granulation results, Mix 4 produced the least reproducible ignitions of the four mixes. Mix 3 again

produced the shortest, yet most irreproducible, ignition times with the large grain propellant.

The results of the ignition effectiveness tests shed some light on the significance of the various igniter characteristics exhibited by the four booster mixes tested. While these results are not conclusive, some observations regarding the results can be made. First, the

booster mix which produced the greatest heat and condensed phase outputs (Mix 3) exhibited the shortest, yet one of the most irreproducible, ignition times. In addition, the booster mix which produced somewhat reduced heat and condensed phase outputs, but higher free oxygen output (Mix 4), exhibited poor ignition results with the large grain propellant, yet quite good results with the small grain propellant. This could indicate marginal ignition functionality, or the need for more exhaustive experimental testing to obtain more statistically meaningful data sample sizes. The results for each of the more oxygen-rich booster mixes (Mixes 1 and 2) were superior to Mixes 3 and 4 for both the large and small grain experiments. Mix 2 produced excellent results for both propellant granulations, showing better overall reproducibility and somewhat shorter ignition times than Mix 1.

There appears to be a rough correlation between the relative ignition times observed for each booster material and the heat outputs for each. The results for both the large and small grain tests show Mix 3 to have the shortest ignition time, Mixes 2 and 4 to have quite similar ignition times, and Mix 1 to have the longest ignition time. This ranking is quite similar to that resulting from the calorimeter heat study. This could indicate a kinetic effect during the ignition, with increased heat accelerating the rate of a rate-limiting reaction. However, this acceleration effect appears to have greater variability if sufficient oxygen production does not also exist. This could indicate that the oxygen acts to further accelerate combustion reactions, so that the continuation of the ignition depends more on heat generated by propellant combustion and less on heat generated by the igniter.

These results do not indicate a significant effect due to the generation of condensed phase products, since Mix 2 produces the smallest fraction of this material but shows perhaps the best ignition characteristics. However, this may indicate that a specific quantity (threshold) of condensed matter is required for good ignition, after which, little effect is realized. In addition, these tests were conducted at

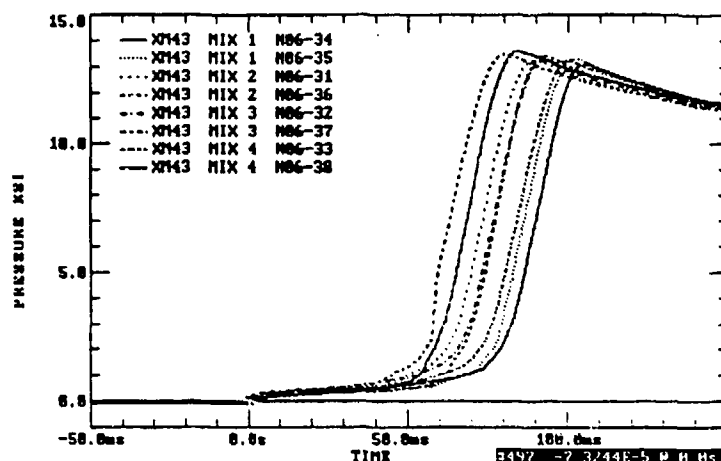


Figure 11- Pressure Data for Ignition of Large Grain HELP1 Propellant With Booster Mixes.

ambient temperature, not at reduced temperature levels where condensed phase output has been shown to be beneficial to achieving good LOVA propellant ignition. At lower temperatures, a greater condensed phase fraction may be required to achieve good ignition than is necessary at ambient conditions. It is also seen that the booster which produces the highest heat output (Mix 3) achieves the most irreproducible ignitions, suggesting that this material is lacking in some key ingredient, such as oxygen. Conversely, the booster which generates the highest free oxygen output (Mix 1) produces acceptable ignitions, but with longer ignition times and slightly less reproducibility than a mix which sacrifices some free oxygen output for more heat generation (Mix 2).

It is possible that the lack of mechanical integrity associated with the igniter flashtubes may, in some way, contribute to the lack of reproducibility in some of the tests conducted. However, the probability of this occurring is not as great as with the calorimeter studies. The igniter effectiveness tests utilized only a single booster pellet. As the discussion regarding the calorimeter testing pointed out, the single-pellet tests resulted in only minimal damage to the flashtube, with the end of each being blown off (i.e. the axial port restriction was removed). While it is desirable that the flashtubes remain undamaged during testing, it is not clear at this time that any damage occurring to the flashtubes resulted in any ignition irreproducibility in the data in Table 6.

Apparently the production of sufficient oxygen as well as sufficient heat content are requirements for achieving good ignition. While both Mix 1 and Mix 2 produce good ignition, the booster with the higher heat output (Mix 2) has a shorter ignition time, again suggesting an acceleration of the chemical kinetics with increased heat. Summarizing, it appears that the optimum booster material contains a complex mixture of ingredients, but necessarily must contain sufficient oxygen and heat outputs, with the condensed phase requirement undetermined at this time.

From the above discussion, it appears that Mix 2 was slightly superior to Mix 1 as a LOVA igniter material, however, it is possible that the experimental configuration used may have played a role in the results obtained. It should be noted that the loading density in a typical gun chamber is about ten (10) times that tested here (approximate 1.0 g/cc versus 0.1 g/cc). Therefore, a much greater amount of molecular oxygen was present, as a result of the large void volume in the bomb, than would be expected in a gun chamber. This may tend to lessen the effect of differences in the free oxygen generated by given booster materials. In other words, the additional atmospheric oxygen may tend to mask the differences in performance between more oxygen rich (Mix 1) and more oxygen poor (Mix 2) booster materials. This issue will be discussed further in the section on combustion gas sampling, where it is seen that atmospheric oxygen can greatly affect the theoretical combustion products at low pressures. Any future work should look at the effect of atmospheric oxygen in these tests, and consider

the use of inert atmospheres such as helium or argon to allow a greater distinction between igniter materials.

### *Combustion Gas Sampling Experiments*

The results for the combustion gas sampling experiments are summarized in Table 7. All of the tests conducted used ignition by a hot-wire, except for run number 60, which utilized an ignition system consisting of two pellets of Mix 1 and a primer. Contained in the table are the actual burst pressure at which the combustion gases were vented, the intended pressure level for the venting, as well as mass ratios for the various component species of interest. These ratios are compared to theoretical values calculated using the NASA-LEWIS code in Figures 12 through 16.

**Table 7. Results From Combustion Gas Sampling Analyses**

Run	Grain size	Pressure (Intended)	Pressure (Actual)	CO/CO <sub>2</sub>	CO/N <sub>2</sub>	H <sub>2</sub> /N <sub>2</sub>	CH <sub>4</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>
51	small	200 (psi)	209 (psi)	1.97	1.50	0.0346	0.209	0.761
52	small	1000	358	2.51	1.24	0.0490	0.0183	0.495
50	small	500	421	1.99	1.04	0.0398	0.00809	0.522
53	small	2000	683	2.62	1.42	0.0613	0.00973	0.542
7	large	200	185	2.60	0.792	0.0161	0.0147	0.305
48	large	500	447	1.75	0.915	0.0639	0.00318	0.523
47	large	1000	570	1.94	1.08	0.0523	0.00595	0.558
4	large	2000	1535	3.63	1.57	0.0766	0.00832	0.433
60*	small	500	346	0.231	0.262	N/A	.00132	1.13

\*This test utilized two pellets of Mix 1 and a primer to ignite the propellant. All other tests utilized hot-wire ignition.

As Table 7 shows, rupture disks rated at 500 psi and lower produced vent pressures which were fairly close to the intended value. However, for rupture disk pressures greater than 500 psi, the actual vent pressure deviated significantly from the intended value. This phenomena is due to the fact that two different types of disk material were utilized. For low burst pressures, aluminum must be used, while at higher pressures, stainless steel is the material of choice. Since aluminum can be ignited by hot

combustion gases, the rupture disks fabricated from this material were purchased with a protective teflon coating. The stainless steel disks had no such coating, since the threat of combustion was not present. The teflon coating appears to have provided thermal insulation, however, allowing the disks to rupture closer to the desired pressure level; while the steel disks appear to have been weakened by heat from the combustion gases, causing failure at lower-than-rated pressures. Any future work in this area will require the use of rupture disks insulated with teflon to allow the desired pressure levels to be attained.

To complement the experimental data, theoretical calculations for the constituent combustion gas products were made using the NASA-LEWIS thermochemical code. Two resulting theoretical plots were made for each component mass ratio, and are presented in Figures 12 through 16 along with the experimental results. The theoretical results were obtained by using very small propellant loading densities (0.001 to 0.010 g/cc), and represent two theoretical

extremes. These small loading densities represent not the initial propellant loading density of the bomb, but merely the propellant burned (at equilibrium) divided by the total closed bomb volume. From this, it is possible to calculate the required (theoretical) mass of propellant to produce the observed pressure. This is accomplished by multiplying the theoretical loading density by the volume of the closed bomb (68 cc). During experimental testing, it was observed that the vast majority of the propellant charge was

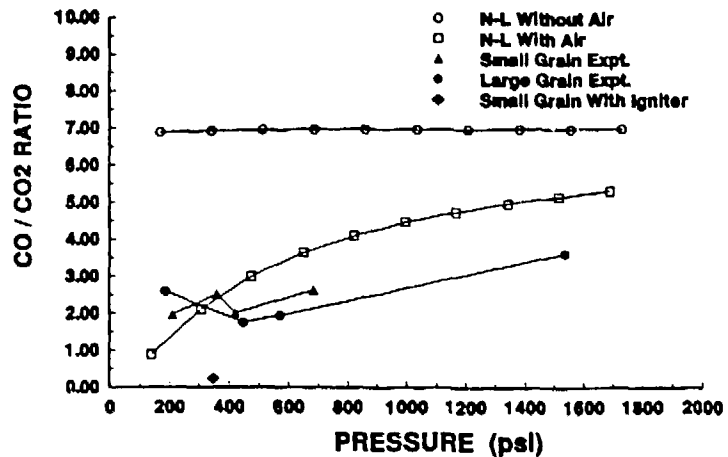


Figure 12- Comparison of Theoretical and Experimental CO/CO<sub>2</sub> Mass Ratios.

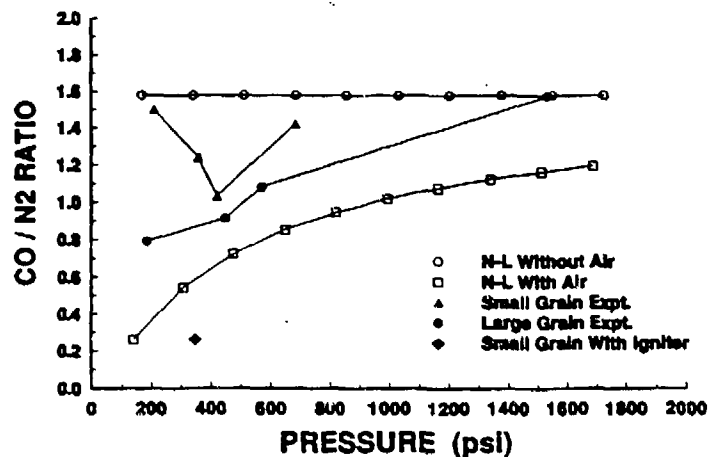


Figure 13- Comparison of Theoretical and Experimental CO/N<sub>2</sub> Mass Ratios.

recovered unburned, with the grain(s) used to ignite the bed showing the majority of the mass loss. Additional propellant was also partially combusted, as indicated by a substantial amount of liquid residue present after a test. This residue material is not predicted by equilibrium calculations, an indication that it is the result of incomplete combustion reactions.

The difference between the two theoretical curves is the presence, or lack, of an atmosphere of air (equivalent to the ullage of the closed bomb) in the combustion calculations. For the calculation which assumes no air, all of the oxygen in the combustion reactions comes from the propellant itself. Conversely, in the calculation which utilizes an atmosphere of air, all of the free oxygen present is assumed to react fully with the mass of propellant consumed. Consequently, the reaction product ratios with air present initially, deviate significantly at low pressures from the calculations which assume no air present, since the mass ratio of free oxygen to propellant is quite high.

As pressure increases, the two theoretical curves converge for each component ratio. This indicates that as more propellant is consumed, the oxygen necessary for combustion comes more from the propellant itself, and the contribution from atmospheric oxygen decreases. Typical thermochemical analyses, for use in closed bomb burnrate reduction, do not account for air present in the closed bomb. However, these calculations are typically done at much higher loading

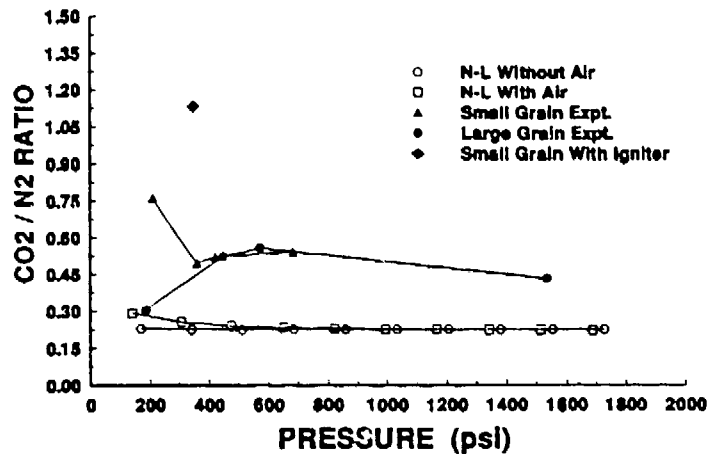


Figure 14- Comparison of Theoretical and Experimental  $\text{CO}_2/\text{N}_2$  Mass Ratios.

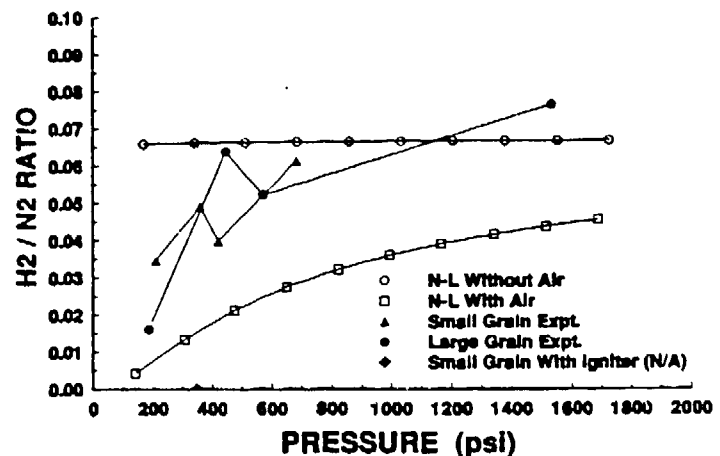


Figure 15- Comparison of Theoretical and Experimental  $\text{H}_2/\text{N}_2$  Mass Ratios.

densities (0.2 g/cc) than those employed here. The higher loading density calculations typically produce pressure levels of 16,000 to 18,000 psi. It is, therefore, reasonable to expect the two theoretical curves, which show significant differences at low pressures, to be indistinguishable at these higher pressure levels.

The experimental results show reasonably good agreement with the theoretical equilibrium results, as Figures 12 through 16 indicate. This similarity with theoretical equilibrium predictions was not anticipated. Due to the nature of the combustion environment during ignition, the experimental results were expected to deviate substantially from equilibrium calculations. However, major deviations from theoretical values are only present in excess amounts of  $\text{CO}_2$  and  $\text{CH}_4$ , indicated by the  $\text{CO}_2/\text{N}_2$  and  $\text{CH}_4/\text{N}_2$  ratios (Figures 14 and 16, respectively). The  $\text{CO}/\text{N}_2$  and  $\text{H}_2/\text{N}_2$  experimental results lie somewhere between the two theoretical curves, possibly where actual equilibrium values might be expected to exist. The deviation in the  $\text{CO}/\text{CO}_2$  ratio is attributable directly to the excess  $\text{CO}_2$ .

The large excess of  $\text{CO}_2$  was not expected, since incomplete (non-equilibrium) combustion typically results in larger CO concentrations. However, while the increased level of the methane ( $\text{CH}_4$ ) concentration does indicate a deviation from equilibrium calculations, the considerable size of this component concentration was not anticipated. As Figure 16 shows, the experimental methane ratio was orders of

magnitude (a factor of about  $10^5$ )

greater than either of the equilibrium

predictions. This is the strongest evidence for non-equilibrium or pyrolysis reactions. Large concentrations of methane (along with hydrogen) are expected if incomplete oxidation occurs. It should be noted that even though the methane ratio is much larger than expected, it still remains a relatively small fraction of the combustion gas products, as depicted by the very small methane (and hydrogen) peak in a typical output from the gas chromatographic analysis, shown in Figure 17. While the figure seems to indicate no significant methane or hydrogen peaks, these peaks are readily apparent when utilizing the GC data analysis package. It is only when attempting to plot the peaks on the same scale with other, substantially larger peak values do they fade into the baseline. The small peaks in question

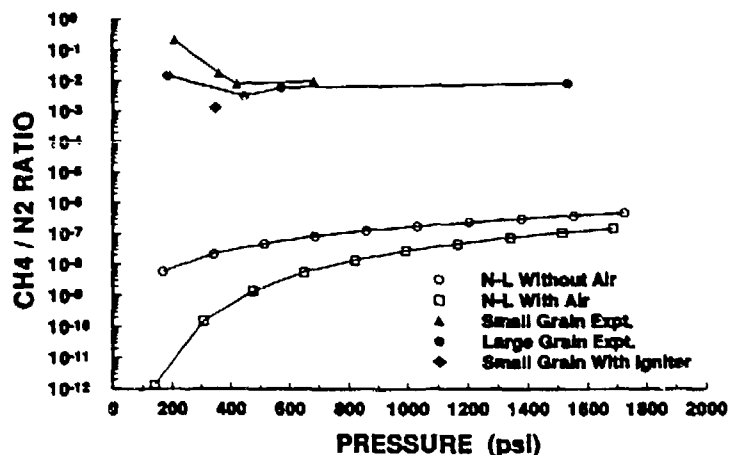


Figure 16- Comparison of Theoretical and Experimental  $\text{CH}_4/\text{N}_2$  Mass Ratios.

do not pose an analytical problem, as the detection limit for these species is still orders of magnitude lower than the magnitude of the methane peak. However, the considerable magnitude of the methane peak could, potentially, draw the quantification of the methane peak into question. It was described in an earlier section how the retention time of each peak was identified. Simple gas chromatographic techniques cannot determine a difference between species which have the same retention time.

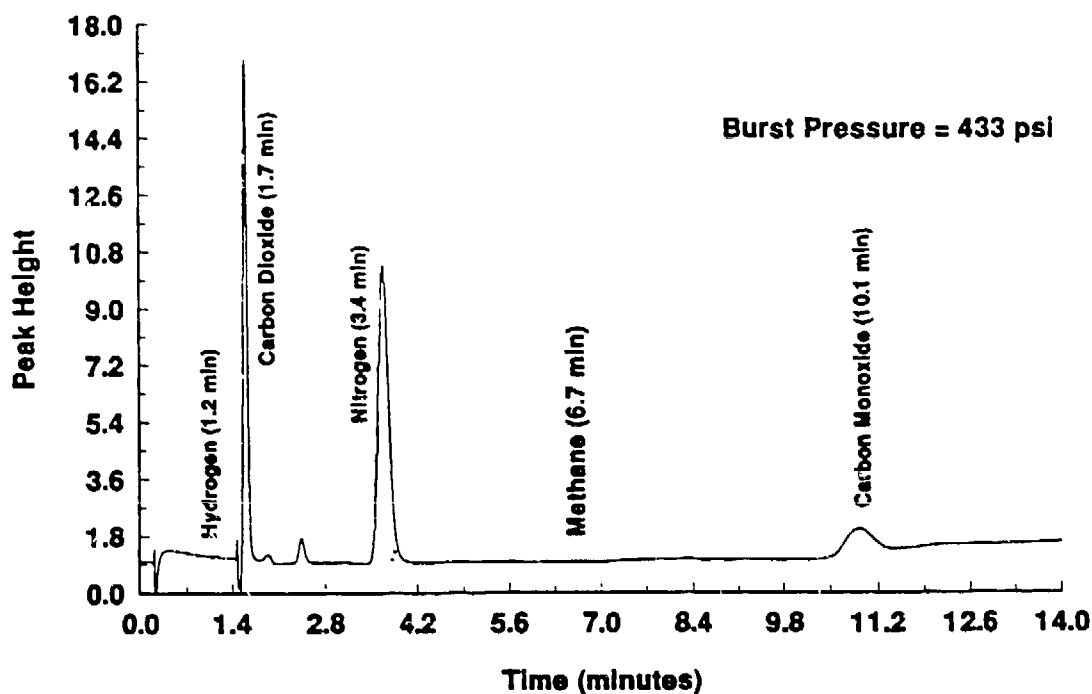


Figure 17- Sample Chromatogram for Gas Sampling Experiments.

Retention time is a function of the relative affinity of each component to the column material. In other words, two species with similar column affinities (a function of polarity and solubility in the column solvent phase) may separate at the same rate and thereby appear as a single peak from the detector. The fact that two columns were used in the present study should act to decrease the probability of this occurrence, still, it cannot be overlooked. The best way to evaluate the identity of a given peak is to utilize an alternate detection method such as mass spectrometry. This technique will allow the mass spectra of each peak exiting the column to be analyzed. This method is routinely used for determination of the purity of given chromatographic peaks and species identification, among other things.

It should be noted that a somewhat analogous investigation, undertaken at the Ballistic Research Laboratory<sup>3</sup> also determined larger  $\text{CO}_2$  and  $\text{CH}_4$  concentrations than predicted by equilibrium calculations. This study utilized Atlas M100 electric matches to ignite XM39 LOVA propellant, rather than the hot-wire method used in this program to ignite the HELP1. The chemical formulations of XM39 and HELP1 are quite similar, indicating that the results should be comparable. The analyses of the combustion products performed at BRL were perhaps more refined than that possible under the scope of the present program (GC-FTIR techniques were utilized to positively identify peaks for a broader range of species). In that study, the reason given for the larger than expected  $\text{CO}_2$  result was that the largest non-equilibrium product, HCN, contains no oxygen. The same may be said for methane and ethane, other major non-equilibrium products found in that study. The large quantities of un-oxidized material present in these experiments suggests that greater quantities of oxygen remain available for the formation of  $\text{CO}_2$  (than predicted by equilibrium calculations).

In addition to the tests conducted with hot-wire ignition, a single test (run 60 in Table 7) was conducted using one of the promising booster materials (Mix 1) determined from the results of earlier testing, along with the OMark 308 primer (0.180 grams), as an ignition source. Two pellets of the Mix 1 booster were utilized to ensure a suitable ignition of the propellant in light of the larger flashtube and relatively low propellant loading density. The booster pellets were staked in place near the primer to limit their freedom of motion and allow proper ignition of the pellets. As mentioned earlier, a different flashtube, 1.5 inches in length and containing eight radial vents with no axial vent, was utilized for this test. With this, the blast from the ignition system was not directed toward the rupture disk, preventing inadvertent and premature venting.

The results of the combustion gas chemical analysis, for the test utilizing the igniter system, are also shown in Figures 12 through 16. As the figures show, the effect of the igniter system, in every case, was to drive the combustion gas ratios in the direction of the equilibrium values. In other words, the effect was to reduce the  $\text{CH}_4/\text{N}_2$ ,  $\text{H}_2/\text{N}_2$  and  $\text{CO}/\text{N}_2$  ratios while increasing the  $\text{CO}_2/\text{N}_2$  ratio. These results demonstrate the expectations for a good igniter system, however, it is believed that the effect might have been even more dramatic had the closed bomb been filled to the loading density of a typical gun chamber (approximately 1.0 g/cc). In this way, a better measure of the effectiveness of an igniter system may be obtained by allowing a larger fraction of the igniter output to contact the propellant bed, assuming the combustion could still be quenched. A higher loading density should provide a better measure of the degree to which the combustion gas chemistry has been altered, as well as to decrease

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<sup>3</sup>J.O. Doali, R.A. Fifer, D.L. Kruczynski, and B.J. Nelson, "The Mobile Combustion Diagnostic Fixture and Its Application to the Study of Propellant Combustion: Part I. Investigation of the Low Pressure Combustion of LOVA XM39 Propellant", BRL Memorandum Report, BRL-MR-3785, August 1989.

the effect of atmospheric oxygen on ignition and low-pressure combustion. In addition, in the present configuration, some of the igniter output may cool from expansion into the large void volume, prior to contacting the propellant, thereby leading to decreased effectiveness. The high loading density test configuration was not utilized during this phase of the program due to concerns regarding the ability to quench the combustion. This could have proved damaging to the gas sampling apparatus. In addition, large amounts of unburned propellant may tend to jam the quick disconnect valve, preventing capture of the gas sample. However, future efforts will investigate the feasibility of utilizing the high-loading density configuration for both hot-wire and igniter-initiated propellant beds.

The results obtained for the combustion gas sampling analyses underscore the importance of oxygen in the ignition of a LOVA propellant formulation (HELP1). A promising igniter system produced a more oxygen-rich environment during ignition, driving the combustion product ratios toward equilibrium values. A qualitative result not mentioned previously emphasizes the sensitivity of the HELP1 formulation to atmospheric oxygen. During efforts to develop a suitable hot-wire ignition system, several wire/power supply configurations were tested in open air to determine their effectiveness in igniting the propellant. On more than one occasion, a candidate hot-wire system, which was successful in igniting a propellant sample in open air, was unable to ignite the propellant when tested in the closed bomb. The only major difference between the two configurations was the amount of free oxygen available to react with the propellant (68 cc versus an unlimited supply). This qualitative observation provided the impetus for the thermochemical calculations with the NASA-LEWIS code which included contributions from atmospheric oxygen.

The actual combustion environment in the hot-wire-initiated closed bomb tests is very complex. While the vast majority of the propellant charge was undisturbed following quenching, the propellant grain(s) utilized to ignite the charge exhibited noticeable regression of the exterior and perforation surfaces. In addition, the grains immediately surrounding the ignition region showed surface regression to a lesser degree. These observations suggest that flamespread plays a role in the experimental results which cannot be properly modeled by a thermochemical code. In other words, while certain localized regions of the propellant bed may be undergoing fairly vigorous combustion, possibly even approaching equilibrium, other broader regions of the propellant are merely undergoing pyrolysis and/or melting reactions as a result of the heat generated by the combustion region. The gas sample obtained, then, will contain the sum total of these reaction products, providing a volume average of the various reaction products.

The utility of the experimental technique outlined in this section will ultimately be shown by the comparison of the results of combustion gas analyses from hot-wire-initiated tests, with those initiated by

various booster formulations. Improved results will be indicated by the magnitude of a shift toward equilibrium ratios (as in Figs. 12 through 16). The scope of work for this Phase One program was such that only a cursory look at this technique was possible, however, future efforts should produce more substantial results.

## IIc. RECOMMENDATIONS

The experimental and analytical program described in this report represents a comprehensive effort covering many aspects of the igniter-propellant (LOVA) interactions. A technique for designing, fabricating and evaluating booster materials for use in igniting a LOVA propellant formulation has been presented. The evaluation of these booster materials includes the relative heat and pressure outputs, the efficacy of propellant ignition, and the effect on propellant combustion chemistry. In addition, a gas sampling technique for evaluation of the combustion gas chemistry was presented and evaluated at a range of pressure levels. The results obtained were quite good and indicate that this technique may be a promising method for development and evaluation of booster materials for LOVA propellant ignition. While additional work is clearly needed, this program has provided a large step toward refining this technique into a viable and useful diagnostic technique.

In light of the results obtained during this program, some recommendations for future work may be made. First, it is necessary to pursue areas where only limited efforts were possible under the scope of the Phase I program. Specifically, propellant combustion gas sampling tests, ignited using various igniter systems, should be conducted. In this way, it will be possible to compare the effects of different booster materials on the combustion gas product ratios. In turn, a correlation between these effects and the efficacy of each booster material in igniting the LOVA propellant (ignition effectiveness testing) may be made. Finally, conclusions regarding the booster chemistry criteria necessary for good LOVA ignition may be drawn as a result.

In addition, in order to obtain a better measure of igniter reproducibility, several repetitions of each experimental set of conditions should be conducted. In this way, statistically meaningful results can be obtained to allow more definitive conclusions to be drawn. In other words, it is necessary to remove systematic errors from consideration if one is to define an igniter system which shows superior reproducibility over other possible systems. Toward this end, possible errors associated with the failure of the flashtube and the position of booster pellets within the flashtube should be minimized. To do this, it will be necessary to produce flashtubes robust enough to survive the testing. The booster pellets should also be staked in place within the flashtube, so that their freedom of motion is reduced. Once all

possible sources of systematic errors have been eliminated, the experimental test conditions should be repeated in series of three (triplicate). Resulting from these tests, the average value and standard deviation of each parameter of interest should be calculated, so that the reproducibility of each igniter system is properly defined.

In order to better establish the effect of free oxygen produced by a booster candidate on ignition effectiveness at low loading densities, it should be investigated whether the ignition effectiveness testing (utilizing the igniter system and propellant bed) should be conducted with an inert atmosphere (i.e. helium or argon). In this way, it is hoped that the effect of free oxygen present in the ullage of the closed bomb can be eliminated, and differences in ignition characteristics resulting from the free oxygen produced by a specific booster formulation better quantified. However, it is recognized that using an inert atmosphere can also affect the thermal conductivity of the gaseous environment, possibly changing the ignitability of a propellant bed. With this in mind, a judicious choice of inert species should be made so that the resulting thermal conductivity matches that of air as closely as possible.

In addition, in order to obtain a more significant evaluation of the effect of the production of condensed phase booster products on LOVA ignition, a series of igniter effectiveness tests may be conducted at reduced (ambient) temperature levels. While the results of the present program do not show a significant effect due to the fraction of condensed phase material produced, it has been shown that at reduced ambient temperature levels large condensed phase products of combustion can have a beneficial effect on ignition effectiveness and reproducibility.

The feasibility of conducting the combustion gas sampling tests using a propellant loading density which more closely resembles that found in a gun chamber (i.e. approximately 1.0 g/cc) should be also be investigated. This may allow a more realistic assessment of the effects of booster chemistry on LOVA propellant combustion (ignition) chemistry, without interference from the additional atmospheric oxygen present in lesser-loaded chambers. In the event that logistical problems associated with a highly-loaded propellant bed, such as the inability to quench the propellant or jamming of the quick-disconnect valve, preclude its use, a helium or argon atmosphere may be substituted for the higher loading density. In this way, the atmospheric oxygen may be completely removed by artificial means. However, the concerns mentioned above regarding the use of inert gaseous atmospheres pertain here, since the thermal conductivity of an inert gas may be significantly different than that of air, the removal of all atmospheric oxygen may alter the heat transfer from the igniter, thereby affecting the performance of the igniter. Also, the location of the propellant bed with respect to the flashtube will be different in propellant beds of low loading density, allowing cooling of the igniter output before contact is made with

the propellant bed. Consequently, this is a less desirable solution than utilizing a fully packed propellant bed, since the igniter-propellant interface still differs from that present in a gun chamber.

The rupture disks used in any future efforts should be teflon-coated, so that they are insulated from the heat of the combustion gases, and as a result are allowed to rupture at higher pressures. It is not believed that the combustion environments at the pressure levels of interest are a threat to ignite the teflon coating.

Finally, the only true test for an igniter system is evaluation within the gun environment. It is therefore necessary to evaluate various prospective igniter systems in an actual gun. If the testing procedures described in this report have merit, the results obtained from these evaluation studies should be comparable to those achieved in the gun system. Once this has been done, and the proper correlations drawn, it should then be possible to develop an igniter system, from many prospective candidates, using only the testing procedures established in this Phase I program. This should result in considerable savings of experimental resources. The final igniter system would then need only limited testing in the gun to prove reliability.

## **APPENDIX**

- NASA-LEWIS Calculations for Booster Materials
- Closed Bomb Pressure Data for Igniter Effectiveness

NASA-LEWIS CALCULATIONS FOR BOOSTER MIX #1  
Constant Pressure Calculation (P=1000 psi)

CHEMICAL FORMULA								WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	STATE	TEMP DEG K		
C	6.0000	H	7.2400	O	10.5190	N	2.7600	0.0000	15.770000	-161640.00	S	298.150	F
BA	1.0000	O	6.0000	N	2.0000		0.0000	0.0000	27.630000	-237110.00	S	298.150	F
AL	1.0000		0.0000		0.0000		0.0000	0.0000	9.240000	0.00	S	298.150	F
K	1.0000	O	4.0000	CL	1.0000		0.0000	0.0000	47.370000	-103430.00	S	298.150	F

O/F= 0.0000 PERCENT FUEL= 100.0000 EQUIVALENCE RATIO= 0.7888 PHI= 0.0000

PHASE CHANGE, REPLACE BAO(S) WITH BAO(L)

THERMODYNAMIC PROPERTIES

P, ATM 68.000  
T, DEG K 2934.7  
RHO, G/CC 1.7382-2  
H, CAL/G -693.27  
U, CAL/G -788.01  
G, CAL/G -4527.42  
S, CAL/(G)(K) 1.3065

M, MOL WT 61.555  
(DLV/DLP)T -1.01148  
(DLV/DLT)P 1.1854  
CP, CAL/(G)(K) 0.4036  
GAMMA (S) 1.1123  
SON VEL, M/SEC 664.0

MOLE FRACTIONS

ALOC1 0.00001  
ALOH 0.00004  
BACL 0.00008  
BACL2 0.01425  
BAOH 0.00015  
BAOH2 0.01299  
CO 0.00922  
CO2 0.16934  
CL 0.00136  
CLO 0.00006  
H 0.00034  
HCL 0.00319  
HOCL 0.00001  
HO2 0.00012  
H2 0.00054  
H2O 0.07076  
H2O2 0.00001  
K 0.00295  
KCL 0.14471  
KO 0.00155  
KOH 0.02869  
K2CL2 0.00341  
NO 0.01737  
NO2 0.00011  
N2 0.08944  
O 0.00545  
OH 0.01431  
O2 0.28738  
AL2O3(L) 0.09249  
BAO(L) 0.02965

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

NASA-LEWIS CALCULATIONS FOR BOOSTER MIX #2  
Constant Pressure Calculation (P=1000 psi)

	CHEMICAL FORMULA	WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	STATE	TEMP DEG K
FUEL	C 6.00000 H 7.24000 O 10.51900 N 2.76000	0.300000	-161640.000	S	298.15
FUEL	BA 1.00000 O 6.00000 N 2.00000	0.229600	-237110.000	S	298.15
FUEL	AL 1.00000	0.076800	0.000	S	298.15
FUEL	K 1.00000 O 4.00000 CL 1.00000	0.393600	-103430.000	S	298.15
O/F= 0.0000 PERCENT FUEL= 100.0000		EQUIVALENCE RATIO= 0.7888		PHI= 0.0000	

## THERMODYNAMIC PROPERTIES

P, ATM 68.000  
 T, DEG K 3204.5  
 RHO, G/CC 1.3433-2  
 H, CAL/G -671.51  
 U, CAL/G -794.10  
 G, CAL/G -5481.26  
 S, CAL/(G)(K) 1.5009  
 M, MOL WT 51.945  
 (DLV/DLP)T -1.02272  
 (DLV/DLT)P 1.4202  
 CP, CAL/(G)(K) 0.6256  
 GAMMA (S) 1.1119  
 SON VEL, M/SEC 755.2

## MOLE FRACTIONS

ALOCL 0.00002  
 ALO2H 0.00019  
 BACL 0.00030  
 BACL2 0.01519  
 BAOH 0.00071  
 BAO2H2 0.02630  
 CO 0.04978  
 CO2 0.25433  
 CL 0.00225  
 CLO 0.00006  
 H 0.00184  
 HCL 0.00561  
 HOCL 0.00001  
 " 0.00016  
 " 0.00308  
 H2O 0.12024  
 H2O2 0.00001  
 K 0.00575  
 KCL 0.09720  
 KH 0.00003  
 KO 0.00202  
 KOH 0.03082  
 K2CL2 0.00080  
 NO 0.01870  
 NO2 0.00007  
 N2 0.10305  
 O 0.00999  
 " 0.02832  
 O2 0.15441  
 AL2O3(L) 0.06874

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

NASA-LEWIS CALCULATIONS FOR BOOSTER MIX #3  
Constant Pressure Calculation (P=1000 psi)

	CHEMICAL FORMULA	WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	STATE TEMP DEG K
FUEL	C 6.00000 H 7.24000 O 10.51900 N 2.76000	0.130300	-161640.000	S 298.15
FUEL	BA 1.00000 O 6.00000 N 2.00000	0.228300	-237110.000	S 298.15
FUEL	AL 1.00000	0.250000	0.000	S 298.15
FUEL	K 1.00000 O 4.00000 CL 1.00000	0.391400	-103430.000	S 298.15
O/F= 0.0000 PERCENT FUEL= 100.0000		EQUIVALENCE RATIO= 1.0243	PHI= 0.0000	

## THERMODYNAMIC PROPERTIES

P, ATM 68.000  
T, DEG K 4511.3  
RHO, G/CC 1.4209-2  
H, CAL/G -572.88  
U, CAL/G -688.78  
G, CAL/G -6634.40  
S, CAL/(G)(K) 1.3436

M, MOL WT 77.349  
(DLV/DLP)T -1.17069  
(DLV/DLP)P 3.3151  
CP, CAL/(G)(K) 1.1611  
GAMMA (S) 1.0781  
SON VEL, M/SEC 723.1

## MOLE FRACTIONS

AL 0.00262  
ALCL 0.00334  
ALCL2 0.00011  
ALH 0.00007  
ALO 0.01426  
ALOCCL 0.00241  
ALOH 0.00088  
ALO2 0.00087  
ALO2H 0.00308  
AL2O 0.00107  
AL2O2 0.00038  
BA 0.00361  
BACL 0.01120  
BACL2 0.02358  
BAOH 0.00705  
BAO2H2 0.00506  
CO 0.13706  
COCL 0.00001  
CO2 0.02078  
CL 0.01548  
CLO 0.00018  
CL2 0.00001  
H 0.04232  
HALO 0.00001  
HCO RAD 0.00001  
HCL 0.00761  
HNO 0.00001  
HOCL 0.00001  
HO2 0.00010  
H2 0.01338  
H2O 0.01815  
K 0.06364  
KCL 0.07549  
KH 0.00091  
KO 0.00952  
KOH 0.01320  
K2 0.00017  
K2CL2 0.00009  
K2O 0.00001  
N 0.00027  
NH 0.00004  
NO 0.02112  
NO2 0.00003

N2	0.07607
O	0.07251
OH	0.04197
O2	0.03766
AL2O3(L)	0.25257

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

NASA-LEWIS CALCULATIONS FOR BOOSTER MIX #4  
Constant Pressure Calculation (P=1000 psi)

	CHEMICAL FORMULA	WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	STATE TEMP DEG K
FUEL	C 6.00000 H 7.24000 O 10.51900 N 2.76000	0.224678	-161640.000	S 298.15
FUEL	BA 1.00000 O 6.00000 N 2.00000	0.393661	-237110.000	S 298.15
FUEL	AL 1.00000	0.131687	0.000	S 298.15
FUEL	K 1.00000 O 4.00000 CL 1.00000	0.249975	-103430.000	S 298.15
	O/F= 0.0000 PERCENT FUEL= 100.0000	EQUIVALENCE RATIO= 0.8652	PHI= 0.0000	

PHASE CHANGE, REPLACE BAO(S)

WITH BAO(L)

## THERMOODYNAMIC PROPERTIES

P, ATM 68.000  
T, DEG K 3607.3  
RHO, G/CC 1.4903-2  
H, CAL/G -670.62  
U, CAL/G -781.12  
G, CAL/G -5604.35  
S, CAL/(G)(K) 1.3677

M, MOL WT 64.871  
(DLV/DLP)T -1.04524  
(DLV/DLT)P 1.7456  
CP, CAL/(G)(K) 0.7022  
GAMMA (S) 1.0961  
SON VEL,M/SEC 711.9

## MOLE FRACTIONS

ALCL 0.00001  
ALO 0.00008  
ALOCL 0.00012  
ALOH 0.00002  
ALO2 0.00002  
ALO2H 0.00069  
BA 0.00006  
BACL 0.00110  
BACL2 0.01369  
BAOH 0.00244  
BAO2H2 0.02541  
CO 0.10152  
CO2 0.15215  
CL 0.00378  
CLO 0.00009  
H 0.00667  
HCL 0.00565  
HNO 0.00001  
HOCL 0.00001  
HO2 0.00019  
H2 0.00659  
H2O 0.08103  
H2O2 0.00001  
K 0.01161  
KCL 0.05874  
KH 0.00009  
KO 0.00340  
KOH 0.02302  
K2 0.00001  
K2CL2 0.00016  
N 0.00001  
NO 0.02607  
NO2 0.00007  
N2 0.12641  
N2O 0.00001  
O 0.02386  
OH 0.04120  
O2 0.11452  
AL2O3(L) 0.13101  
BAO(L) 0.03847

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

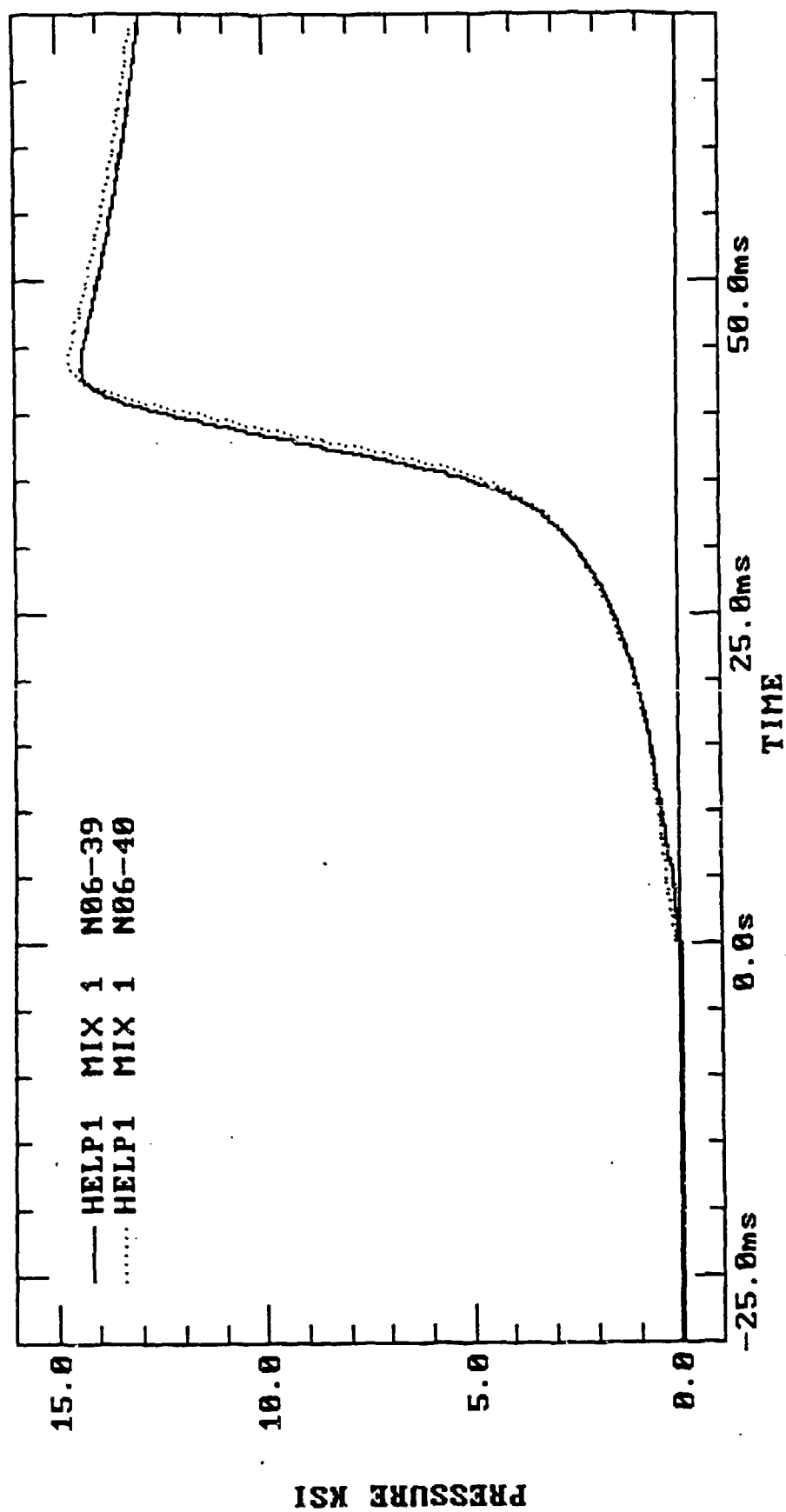


Figure A1- Ignition of Small Grain HELP1  
Propellant With One Pellet of Mix 1

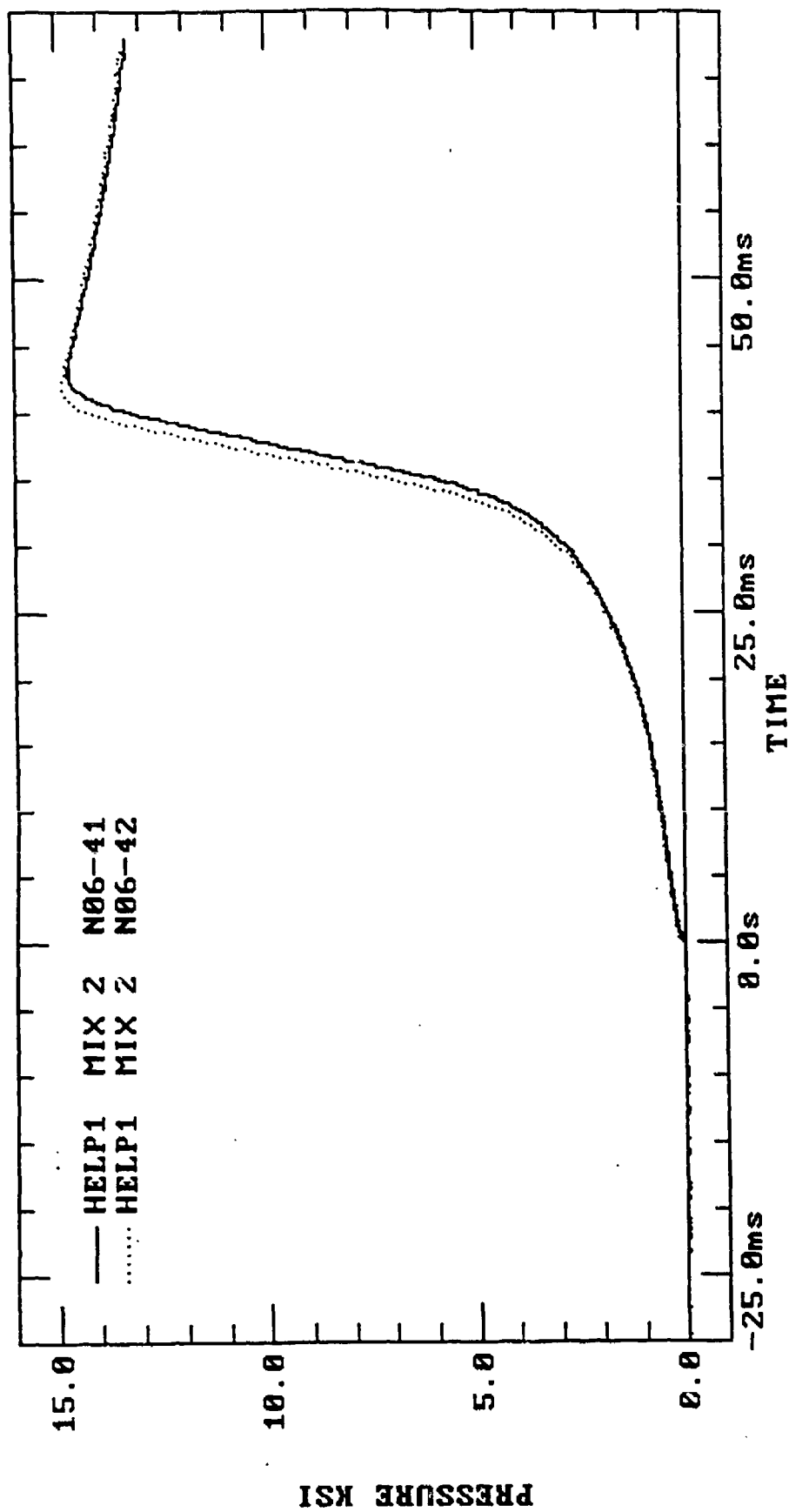


Figure A2- Ignition of Small Grain HELP1  
Propellant With one Pellet of Mix 2

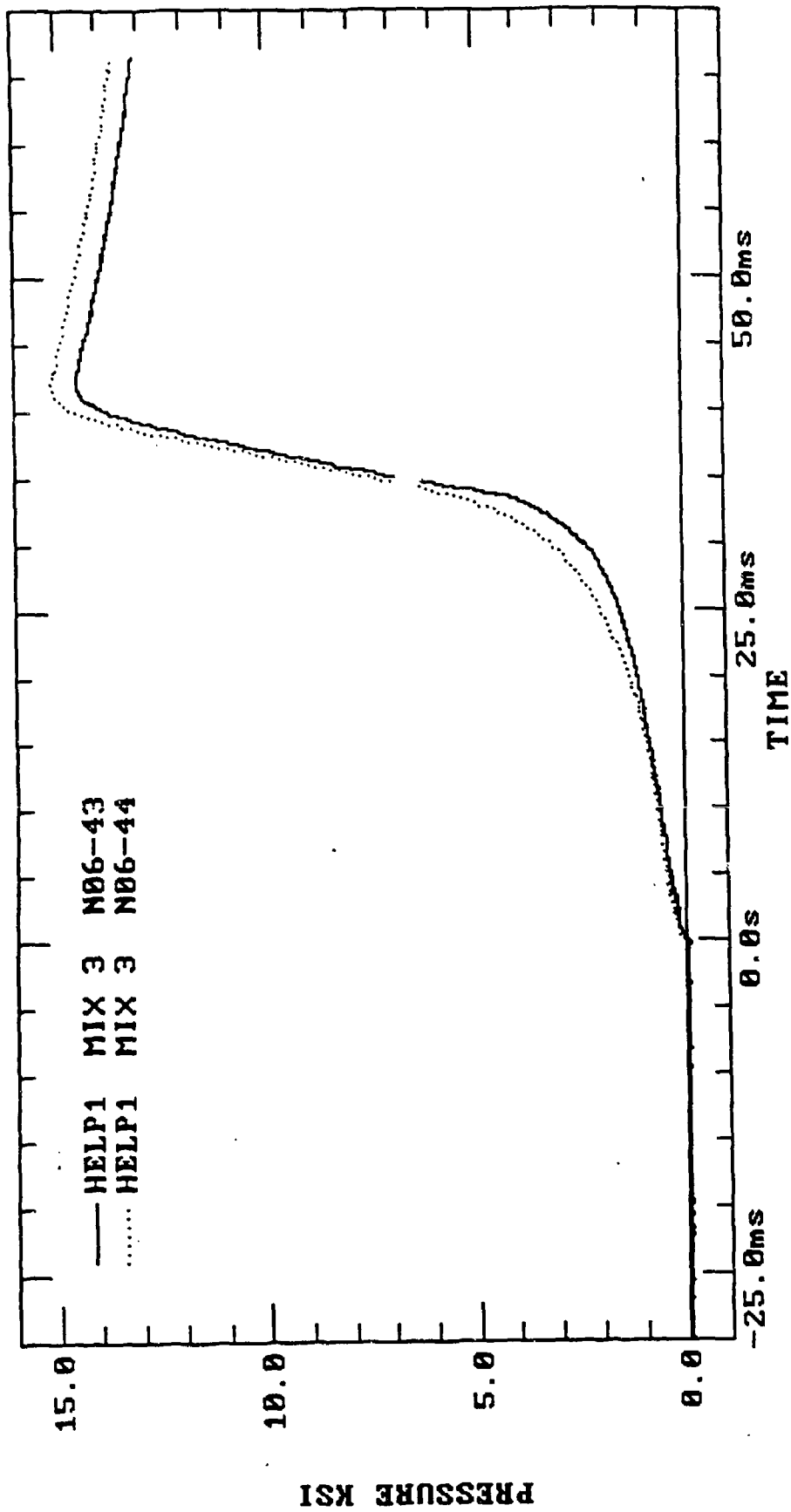


Figure A3- Ignition of Small Grain HELP1  
Propellant With one Pellet of Mix 3

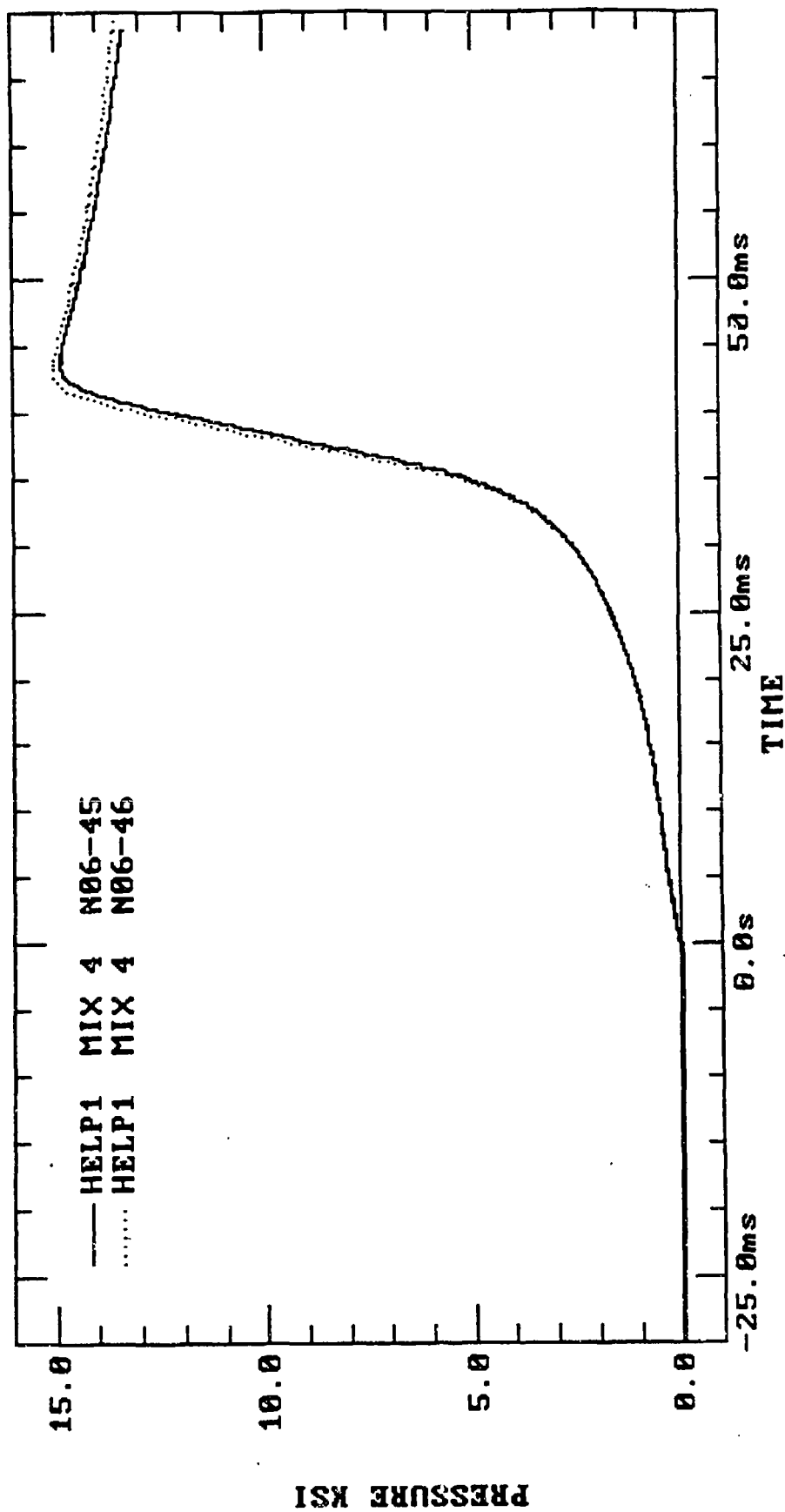


Figure A4- Ignition of Small Grain HELP1  
Propellant With One Pellet of Mix 4

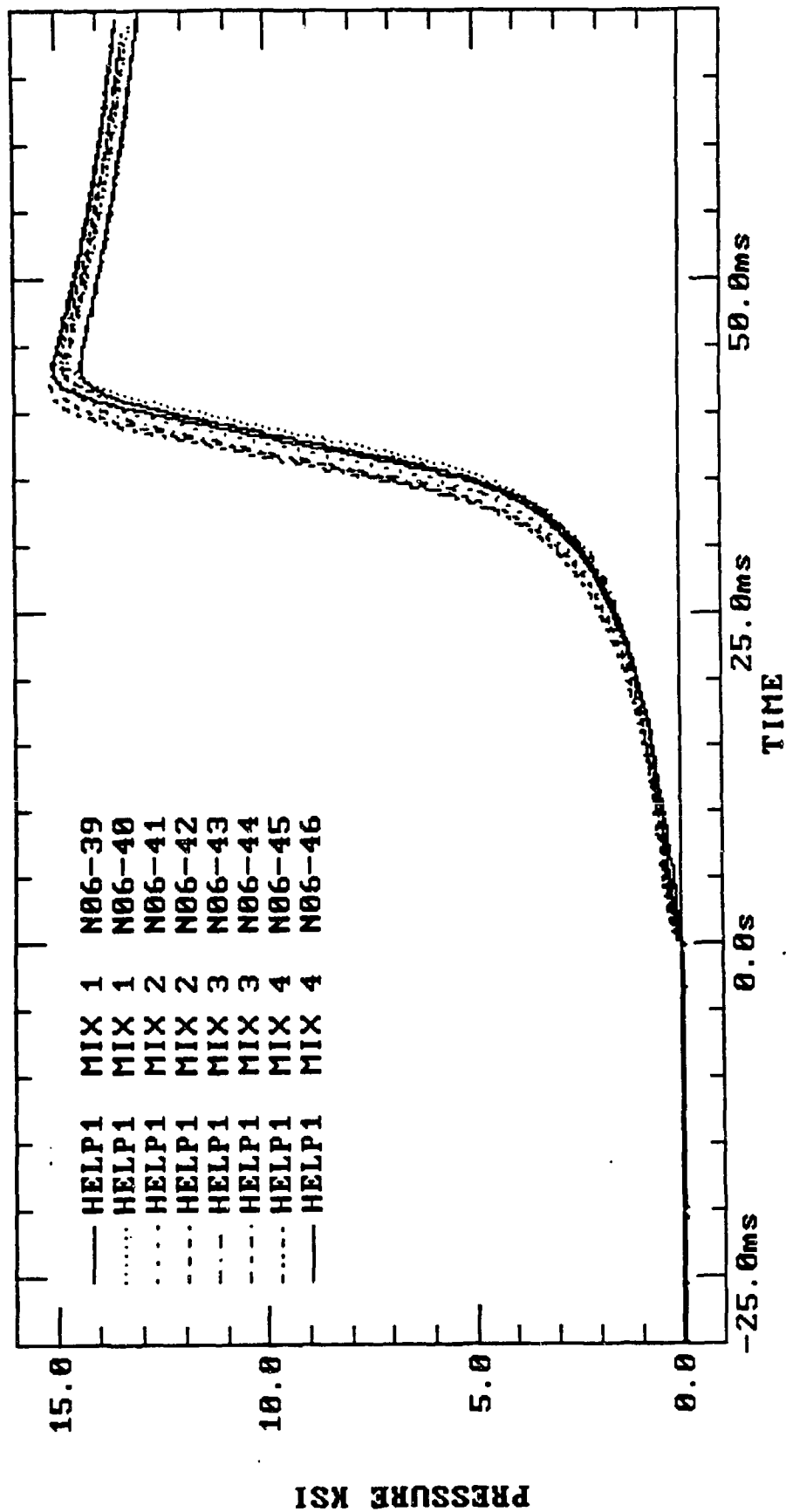


Figure A5- Comparison of Ignition of Small Grain  
Propellant With One Pellet of Booster Mixes

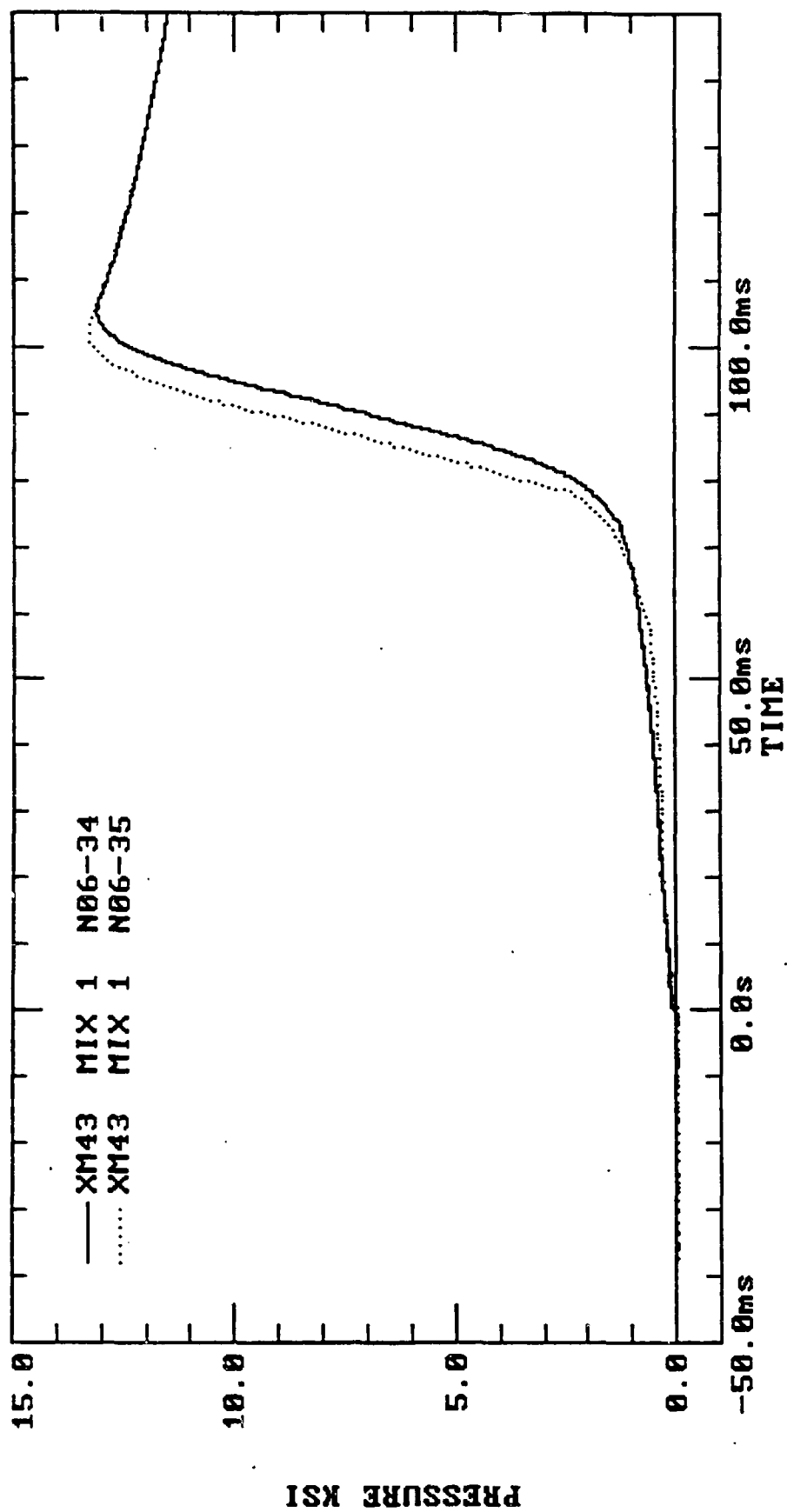


Figure A6- Ignition of Large Grain HELP1  
Propellant With One Pellet of Mix 1

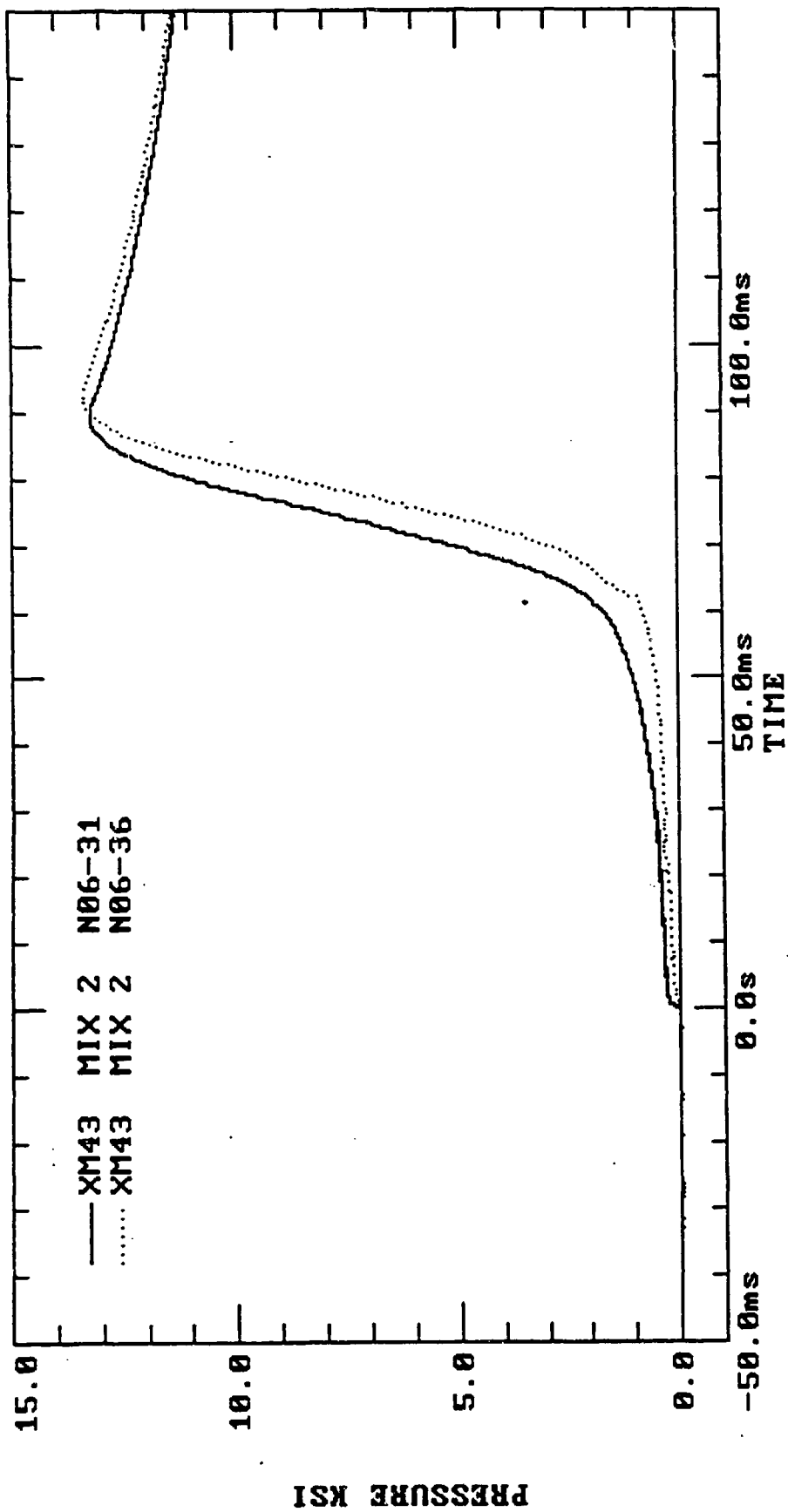


Figure A7-- Ignition of Large Grain HELP1  
Propellant With One Pellet of Mix 2

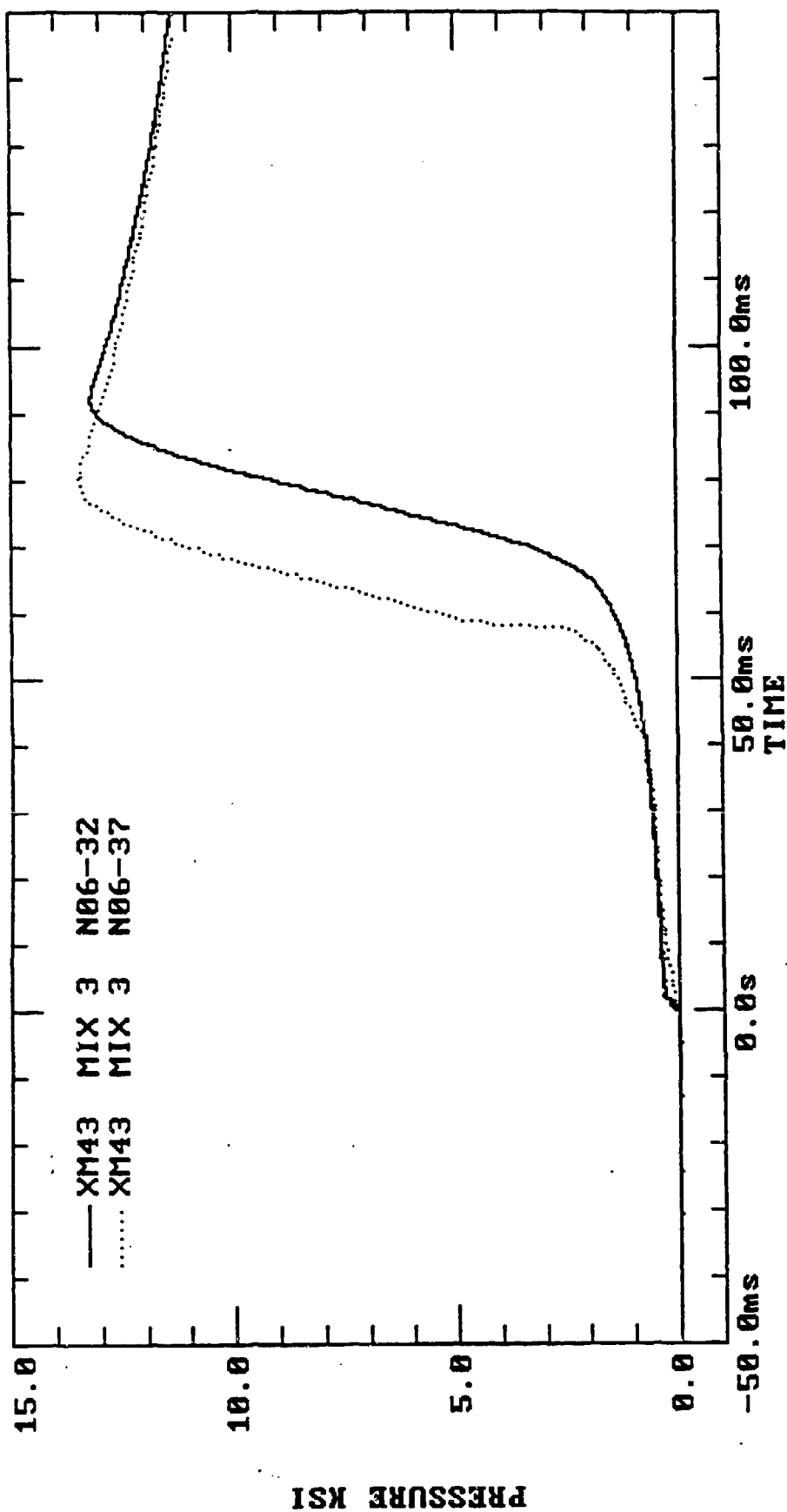


Figure A8- Ignition of Large Grain HELP1  
Propellant With One Pellet of Mix 3

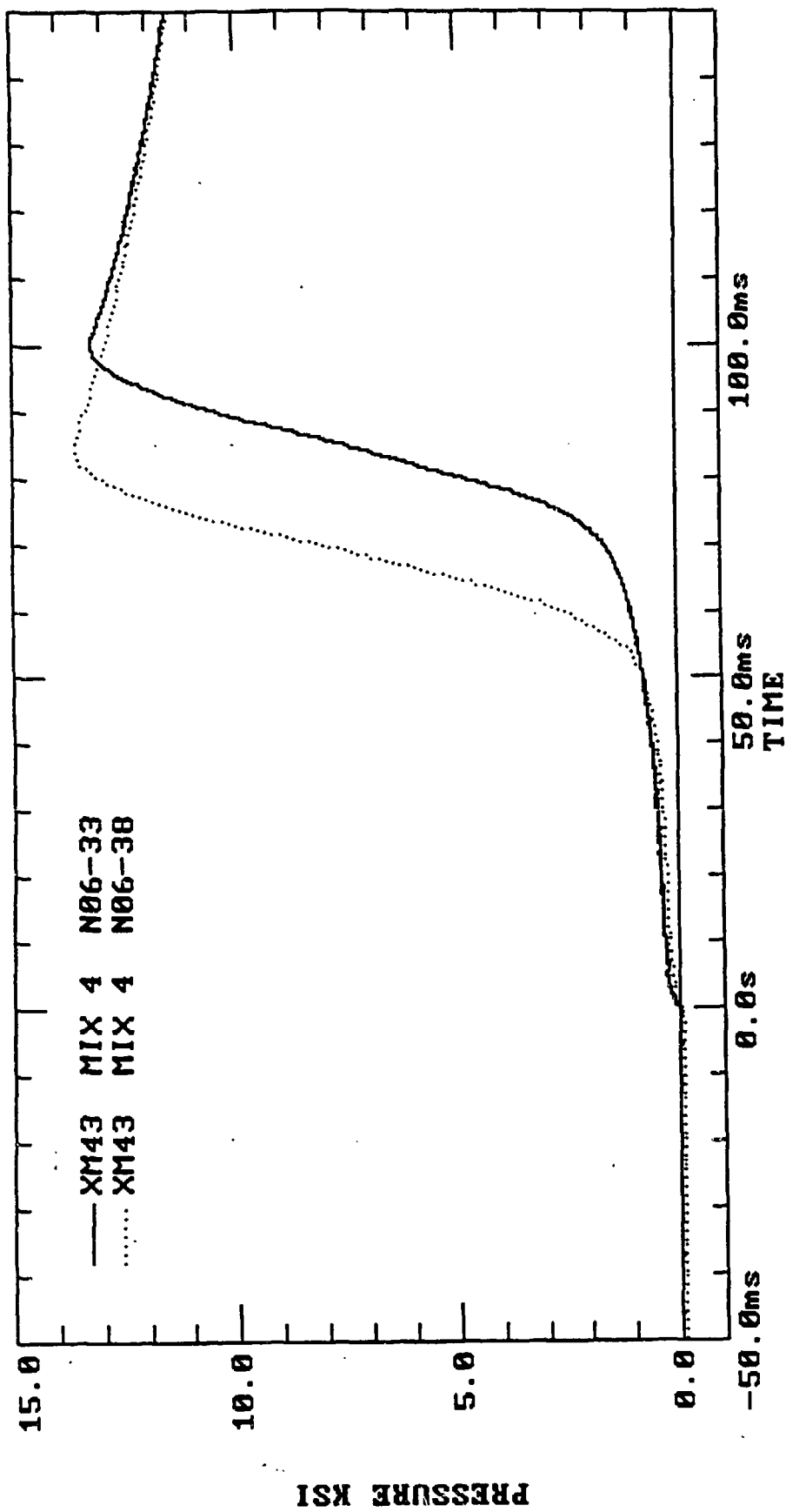


Figure A9- Ignition of Large Grain HELP1  
Propellant With One Pellet of Mix 4

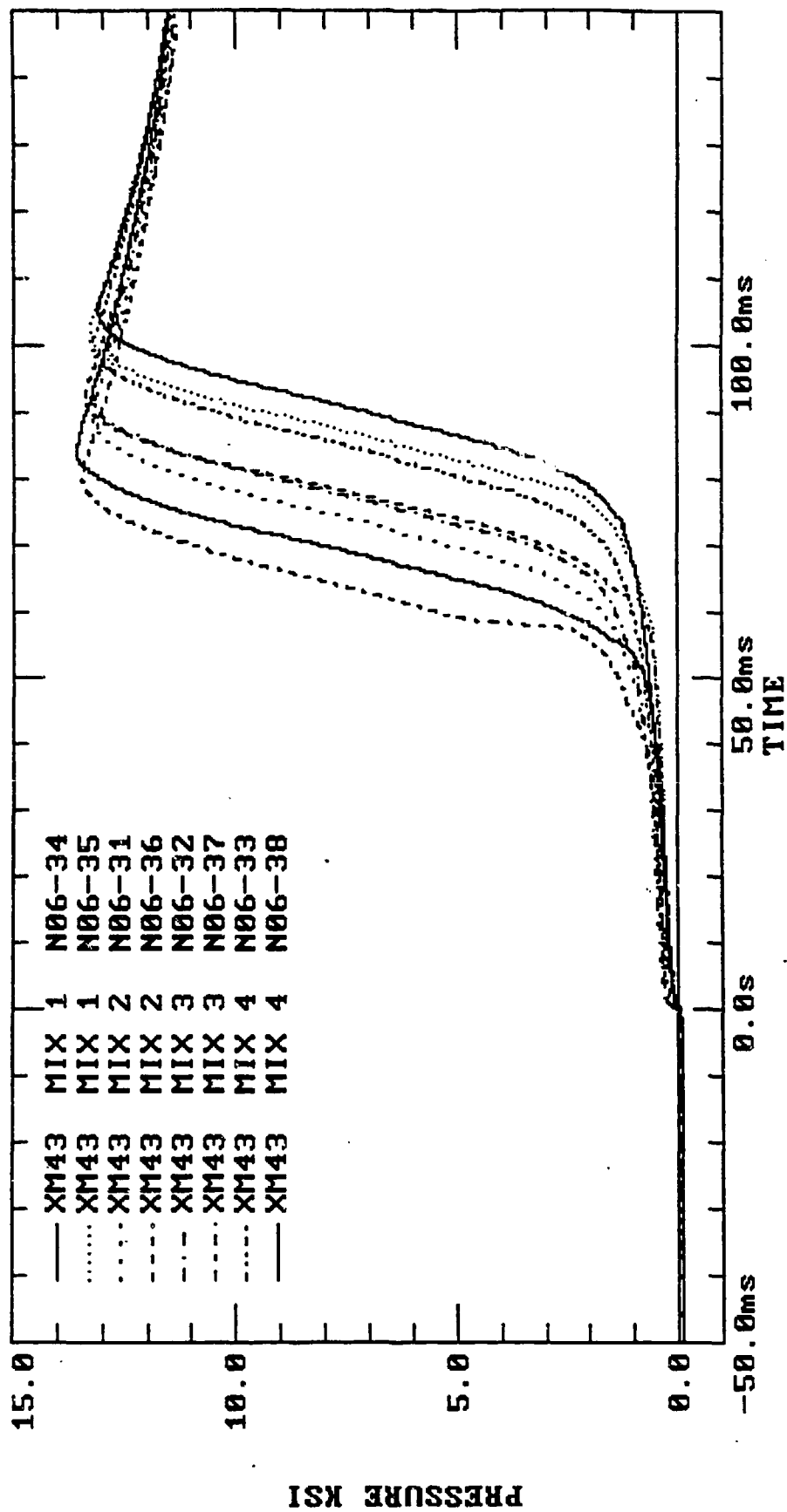


Figure A10- Comparison of Ignition of Large Grain  
Propellant With One Pellet of Booster Mixes

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